

# Compatibility Assessment of Plastic Infrastructure Materials to Test Fuels Representing Gasoline Blends Containing Ethanol and Isobutanol

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## Abstract

The compatibility of plastic materials used in fuel storage and dispensing applications was determined for test fuels representing gasoline blended with 25 vol.% ethanol and gasoline blended with 16 and 24 vol.% isobutanol. Plastic materials included those used in flexible plastic piping and fiberglass resins. Other commonly used plastic materials were also evaluated. The plastic specimens were exposed to Fuel C, CE25a, CiBu16a, and CiBu24a for 16 weeks at 60°C. After measuring the wetted volume and hardness, the specimens were dried for 65 hours at 60°C and then remeasured for volume and hardness. Dynamic mechanical analysis (DMA) was also measured on the dried specimens.

The plastic materials used as permeation barriers exhibited the least amount of property change when exposed to the test fuels. The performance of nylon was highly dependent on the grade; of the four nylons evaluated, Nylon 6 and Nylon 6,6 showed the lowest property change following exposure to Fuel C, CiBu16a and CiBu24s, but swelled over 7% when exposed to CE25a. Acetal and polybutylene terephthalate (PBT) swelled around 5% with exposure to the test fuels, while high density polyethylene (HDPE) swelled around 10% for each test fuel. The remaining thermoplastics swelled to higher values and in the case of polypropylene, dissolution occurred with exposure to CE25a. The fiberglass resins experience more swelling in CE25a than with the Fuel C or the two isobutanol blends. In general, the plastics exhibited a positive volume change when dried, which was attributed to fuel retention. In addition CE25a produced a higher degree of property change than the other test fuels.

## 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.<sup>1</sup> Until recently, the amount of ethanol that may be blended and sold in the USA as an additive to gasoline had been limited to 10% by volume (E10) by the US Environmental Protection Agency (EPA). This concentration corresponds to the 3.7wt.% requirement allowed under the approved OCTAMIX waiver.<sup>2</sup> 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. 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.<sup>3</sup> In 2008, the US Department of Energy (DOE) initiated a series of studies to investigate the impact of fuel ethanol on materials common to fuel storage and dispensing infrastructure.<sup>4,5</sup> In general, plastics are used in structural applications (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 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.

Ethanol is the most common biofuel, but other biofuels, such as isobutanol, are also being considered as gasoline additives. In fact, Butamax Advanced Biofuels, LLC has developed proprietary technologies to convert corn into isobutanol using the infrastructure already in-place at ethanol production facilities.<sup>6</sup> Isobutanol is of interest since it has a higher energy density relative to ethanol. It is also less volatile and water soluble.

The focus of this investigation was to compare the compatibility of fuelling infrastructure materials to test fuels representing E10 and E15 and their corresponding oxygen equivalents with isobutanol (iBu16 and iBu24). This paper describes a research project at Oak Ridge National Laboratory (ORNL), supported by Butamax, to perform empirical studies using aggressive fuel formulations representing 16 and 24% isobutanol. Another

objective was to perform a solubility analysis for each material type and fuel formulation for common infrastructure plastic materials. These 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.

## Solubility and Its Impact on Other Plastic Materials Properties

For polymer, fuel compatibility is predominantly determined by the mutual solubility between the polymer and fuel. In practice, the degree, or extent, of solubility, is assessed by measuring the volume expansion of the elastomer. 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.<sup>7</sup>

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 parameters for mixtures of ethanol concentration increases from 0% to 15%, the solubility parameter of the fuel approaches the values of many polymers and, therefore, the potential for higher solubility, and hence polymer swelling and possible deformation, is also enhanced. For ethanol concentrations between 15% and 49%, high solubility, and therefore peak swell, is predicted for many polymers. Another consideration is that polymer materials used in the fuelling infrastructure are complex compositions of one or more polymers (or copolymers) and 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.

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.

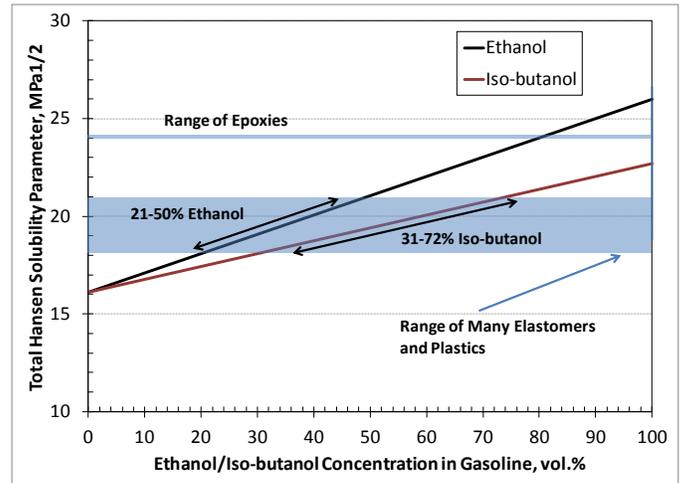


Figure 1. Total solubility parameter curves for gasoline blended with ethanol or isobutanol.

## Materials, Equipment and Procedure

### Test Fuels

In this study test fuels representing gasoline blended with 25% ethanol were prepared along with blends containing 16% and 24% isobutanol. These fuels, denoted as CE10a, CE15a, CiBu16a and CiBu24a, were based on the Fuel C formulation in SAE J1681. The aggressive ethanol also followed the SAE J1681 protocol; however, this protocol does not cover butanol.

The aggressive formulation is conservative by design but is 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.

These test fuels are designed to simulate severe, real-world conditions. They are also intended to minimize the exposure time necessary to rigorously evaluate materials while providing a standard method of testing fuel system materials. Fuel C was selected as the control since it represents premium gasoline and is a widely used standard test fluid for studying material compatibility to gasoline.

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 30-gal 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.<sup>8</sup> 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 aggressive ethanol, 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 1 liter 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.

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

### 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 nylon and HDPE, which 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 identified by the survey results as infrastructure materials, are so widely utilized that the likelihood is high that they are, in fact, used in some infrastructure applications. 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.

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, then they were removed and measured for volume, mass, and Shore D hardness while in the wetted (or saturated) state. Once the wetted properties were measured, the elastomers 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.

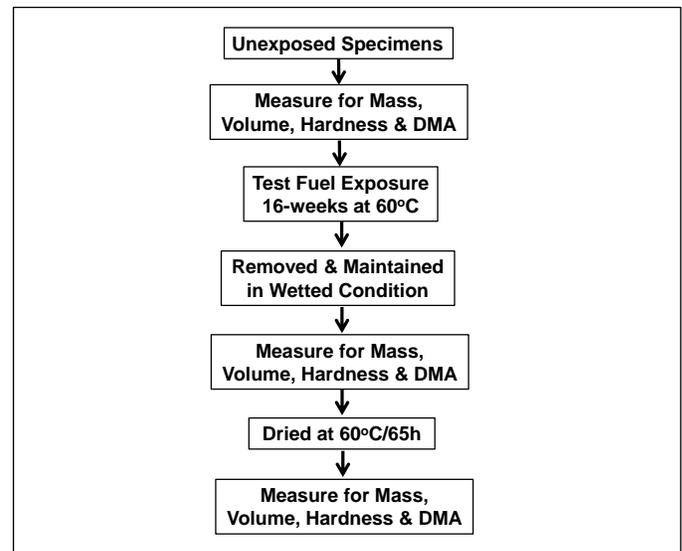


Figure 2. Flow chart showing the exposure protocol and test methods.

Dynamic mechanical analysis (DMA) testing was also performed to further evaluate whether any structural changes had taken place in the polymers following exposure to the test fuels that could not be detected from the mass, volume, and hardness measurements. Dynamic mechanical analysis measures the storage modulus as a function of temperature and is used to determine the onset of the glass to rubber transition of polymers.<sup>9</sup> A simplified representative DMA graph is shown in Figure 3. At low temperatures, all polymers will be in a rigid glassy state due to molecular binding. As the temperature increases a point will be reached whereby the molecular structure is “relaxed”. At this point the polymer molecular chains become more flexible and the material modulus transitions to a more pliable rubbery state. The temperature associated with this onset is known as the glass transition temperature,  $T_g$ . Resins are designed to withstand deformation and, as a result, their operational range is limited to the glassy region as shown. This is in marked contrast to elastomer materials which are designed to flex (their operational range is in the transition zone to the rubbery region).  $T_g$  is an important property since it is sensitive to any microstructural change that has occurred to the polymer structure. The shift in  $T_g$  is also important since it (along with the melting point) defines the range of operation for an

elastomer. If  $T_g$  is decreased, then the operational range of plastic materials decreases as well.

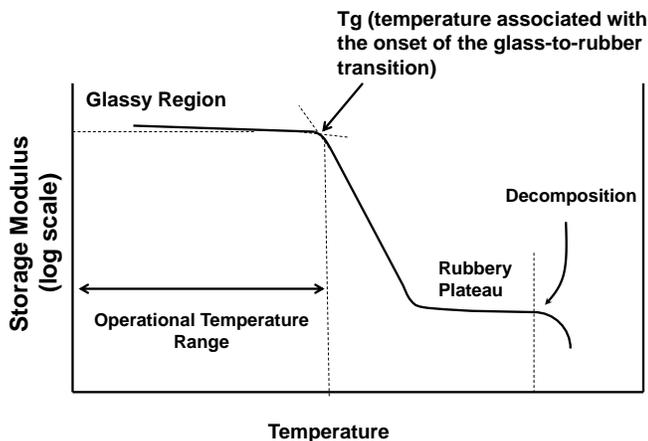


Figure 3. Representative DMA results for a polymer material.

## Results

### Solubility Analysis

A solubility analysis was performed for the elastomer materials with fuel blends representing gasoline (Fuel C), gasoline blended with 25% ethanol (CE25a), gasoline blended with 16% isobutanol (CiBu16), and gasoline blended with 24% isobutanol (CiBu24). The analytical approach was based on the Flory-Huggins model using the Hansen solubility parameter (HSP) methodology. This type of analysis is useful in predicting swelling behavior in polymeric materials exposed to known solvents. It is important to note that the aggressive components were added in trace quantities, and are not expected to affect solubility. Likewise water is expected to have little, if any, impact as well. Relative volume swell was assessed by determining the solubility distance ( $d_s$ ) for each material type as a function of alcohol content and comparing these values to the interaction radius (IR) of the polymer. The interaction radius represents the zone of high solubility for a given polymer and is independent of solvent type. If the solubility distance falls within (or is less than) the interaction radius, then moderate to high solubility can be expected. Materials exhibiting distances roughly equivalent to the interaction radius would be expected to produce low to moderate solubility, while distances higher than the interaction radius would predict negligible to low solubility. The difference between the interaction radius and the calculated solubility distance for each fuel and material combination is shown in Figure 4. Since volume swell corresponds to solubility, these results indicate that the majority of the plastic materials should exhibit very low to moderate swelling. The plastics which show the highest susceptibility to volume swell are PTFE, PETG, PP, and the polyester resins. This analysis also indicates that (in general) higher swelling should be observed for the test fuels containing the added alcohols, and that CE25 may produce more swelling than either CiBu16 or CiBu24.

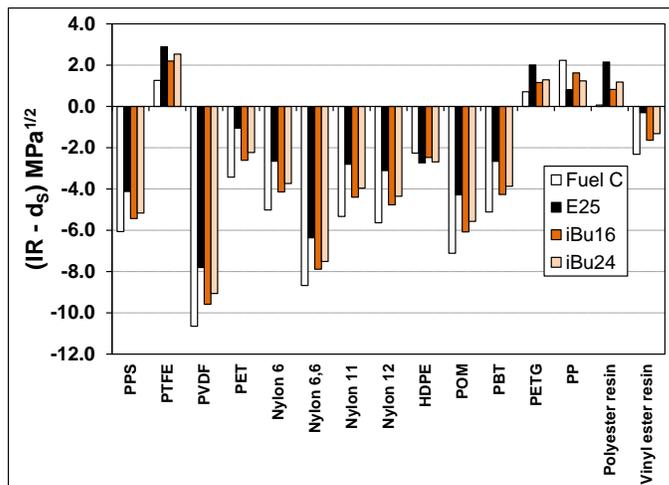


Figure 4. Solubility analysis results summary for the plastic materials.

### Permeation Barrier Materials

#### Volume Change

The wet volume increase for the four permeation barrier plastic materials was relatively low as shown in Figure 5. As predicted by their respective solubility curves, the PPS, PET, and PVDF specimens did not undergo significant mass or volume swell with exposure to the test fuel liquids. In contrast, the solubility result for PTFE (Figure 4) indicated that moderate swelling would have occurred for this material in the test fuels, but that was not the case as PTFE showed negligible swelling. The implication is that the Hansen solubility parameters for PTFE were not accurate for this particular grade.

Of the four barrier materials, PVDF exhibited the most swell with the test fuels, although the extent was quite low. The mass was raised 0.5% with exposure to each of the test fuels, but the volume varied according to fuel type. Fuel C produced a 1.5% volume increase, and the additions of aggressive ethanol and isobutanol further increased swelling by 5 and 3%, respectively.

As shown in Fig. 6, the permeation barrier plastics exhibited slight volume increases with the test fuels after being dried. For PPS, PET, and PVDF, the relative volume increase tracked with the relative mass increase. However, for PTFE, the Fuel C formulation produced the highest mass increase and the lowest volume expansion of the test fuels. Both PET and PVDF incurred noticeably higher mass and volume gains with CE25a than with the other test fuels.

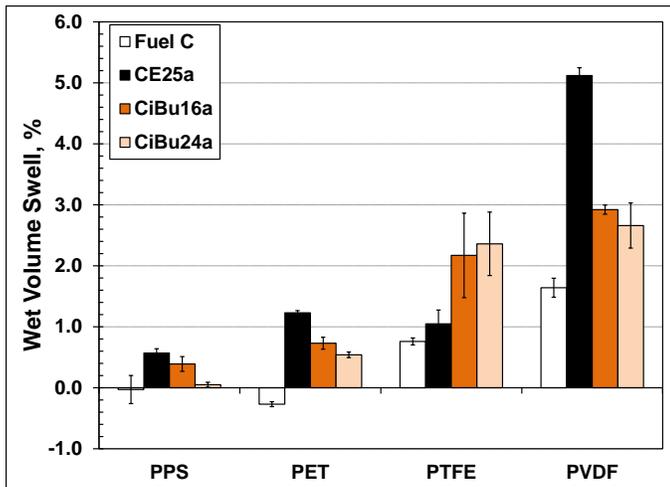


Figure 5. Wet volume swell results for the permeation barrier plastics. Specimens were submerged in the test fuels for 16 weeks at 60°C.

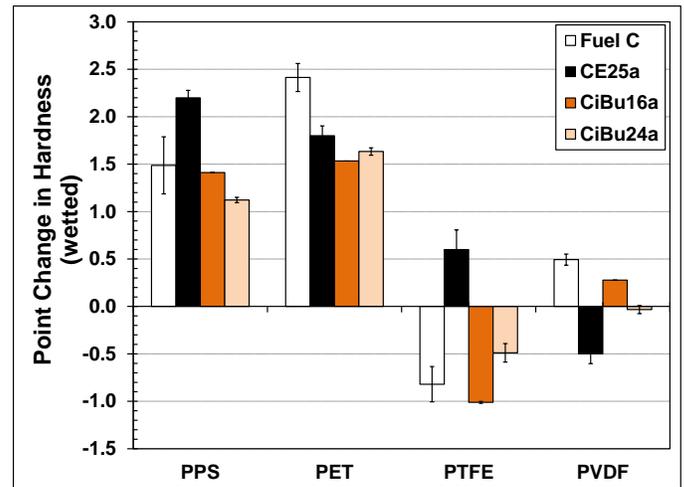


Figure 7. Point change in wet hardness results for the permeation barrier plastic specimens. Specimens were submerged in the test fuels for 16 weeks at 60°C.

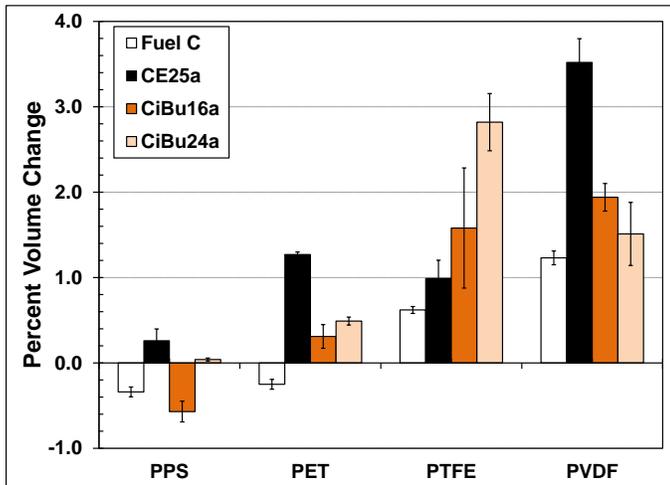


Figure 6. Volume change results for the permeation barrier plastic specimens after drying at 65°C for 60 hours.

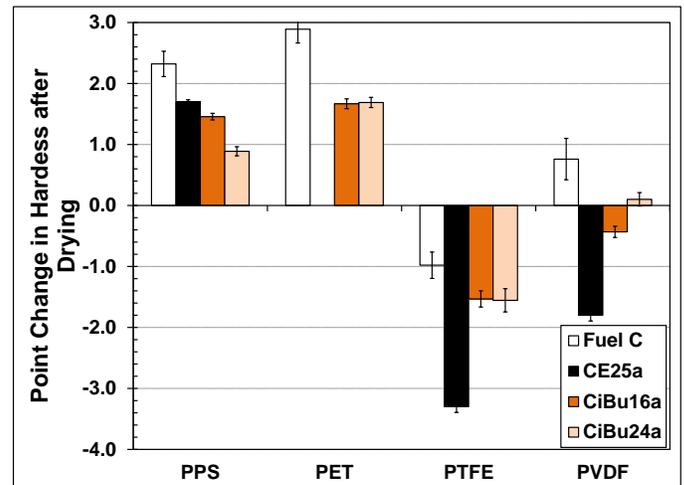


Figure 8. Point change in hardness results for the permeation barrier plastic specimens after drying at 60°C for 65 hours.

### Point Change in Hardness

The point change in hardness results for the permeation barrier plastics are shown in Figures 7 and 8 for the wet and dried conditions, respectively. Each of these materials exhibited essentially negligible change in hardness (whether wet or dry) as demonstrated by the fact that the point changes are all within  $\pm 3$  points from the original baseline condition. This result is not surprising since the original volume changes (while in the wetted state) were low for these materials.

When dried, the measured hardness for these materials showed slight deviations from the baseline value. CE25a did cause a slight additional softening in PTFE and PVDF, but the change in hardness did not appear to be affected by the addition of isobutanol.

### Transition Temperature

The influence of fuel chemistry on  $T_g$  for permeation barrier plastic materials is shown in Figure 9 for liquid- and vapor-phase exposures. Except for CE25a, the  $T_g$  values for the four plastic types were not significantly changed with exposure to the test fuels and isobutanol appears to have no detrimental effect. The most notable shift in  $T_g$  occurred for the PET specimen. This effect was not expected based on the other property changes for this material, but it does indicate that some level of micro-structural change had occurred. PET, when exposed to CE25a over a long period, did experience a 30°C drop in  $T_g$  with exposure, and the implication is that PET exposed to ethanol will be in the rubbery state at high ambient temperatures instead of in the desired rigid condition. This result is a strong indication that chemical changes had occurred in the polymer. The results for the specimens exposed to the vapor phase roughly parallel the results

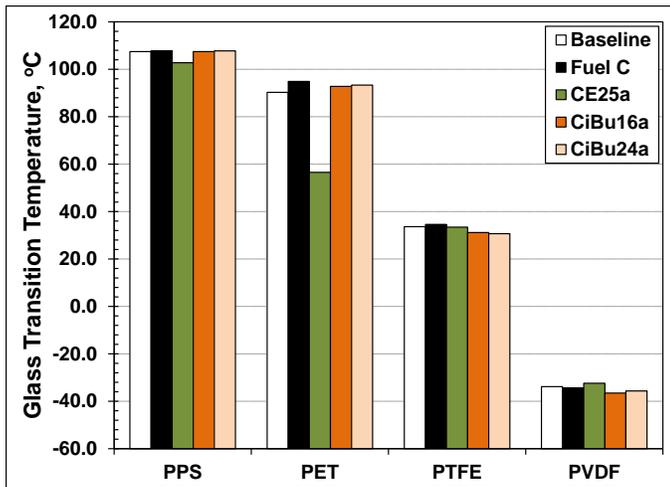


Figure 9. Glass transition temperature results for the permeation barrier specimens after drying at 60°C for 65 hours.

## Nylon and HDPE

### Volume Change

The wet volume changes for the nylon and HDPE specimens are shown in Figures 10 and 11, respectively. The solubility analysis (summarized in Figure 4) predicted these materials to be insoluble with the test fuel formulations. However, moderate solubility was observed following exposure to CE25a. Nylons 6 and 6,6 exhibited similar behavior as they both demonstrated negligible swelling with Fuel C, CiBu16a, and CiBu24a, which is consistent with the solubility analysis. However, CE25a produced a 7.5 to 10% increase in swelling in these two nylon grades. The other petroleum-based nylon material was Nylon 12, which was also unaffected by Fuel C; however, the addition of 25% aggressive ethanol caused its volume to expand over 9%. CiBu16a and CiBu24a produced a slightly lower volume expansion (7%). Bio-derived Nylon 11 differed from the petro-nylons in that the volume expanded 5% with exposure to Fuel C. Adding 25% ethanol further expanded the volume to 18%, while isobutanol produced a slightly lower 15% volume increase.

The volume increases for HDPE were essentially the same for all test fuels, an indication that Fuel C was primarily responsible for this effect. The mass increase was around 7%, and the volume was only slightly higher at around 8%. These increases are small but significant; they do indicate that the addition of ethanol and isobutanol to gasoline will not further increase mass and volume.

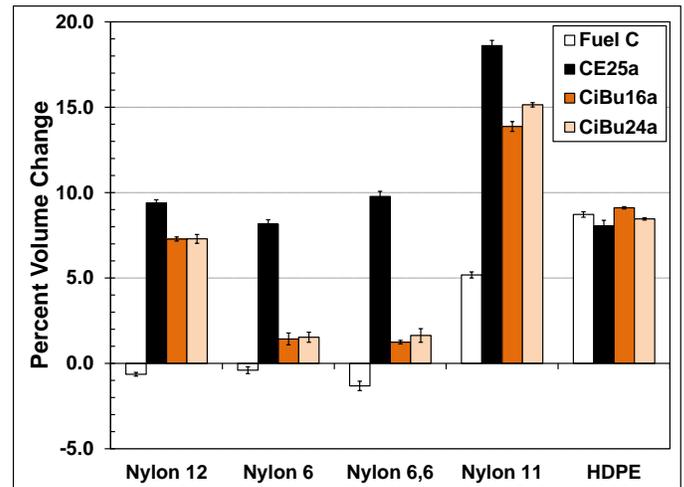


Figure 10. Wet volume swell results for four nylons and one HDPE material. Specimens were submerged in the test fuels for 16 weeks at 60°C.

The dried volume change results (from baseline) are shown in Figure 11 for the four nylons and HDPE. HDPE essentially returned to its original volume after being dried. The nylon results varied according to fuel formulation and type of nylon. Consistent with other measured properties, Nylon 6 and Nylon 6,6 performed similarly. For both materials, the volumes returned to their original values after being exposed to Fuel C and the fuels containing isobutanol. In marked contrast, 25% aggressive ethanol was observed to produce a small increase in volume. Nylon 12 was unusual in that it lost significant volume after being dried. Most of this loss can be attributed to Fuel C, but ethanol produced a small additional contribution. The dried Nylon 11 specimens showed a small (4%) increase in the volume following exposure to Fuel C, and the isobutanol fuels raised the mass to between 5 and 6% and the volume to around (8%). For this material, ethanol produced the lowest property change (~2%) from the original baseline condition.

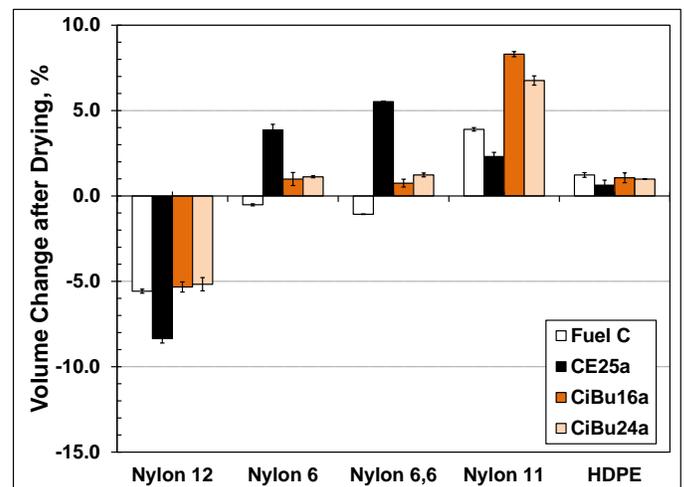


Figure 11. Volume change results for four nylons and one HDPE material after drying at 60°C for 65 hours.

## Point Change in Hardness Results for Wet and Dry Conditions

The wet hardness results for the nylons and HDPE specimens are shown in Figure 12. Nylon 12 hardness was unaffected by Fuel C, but was slightly softened 5 to 7 points with exposure to the test fuels containing ethanol or isobutanol. Nylons 6 and 6,6 exhibited similar behavior with ethanol, but exhibited a 7 point increase with exposure to fuel C. These two nylons exhibited a lower amount of hardening for the fuels containing isobutanol, and they were both slightly softened when exposed to CE25a. Nylon 11, which was bio-based, exhibited negligible change for Fuel C; however, the added ethanol and isobutanol dropped the hardness by 17 and 10 points, respectively (a substantial degree of softening). HDPE showed a small, but consistent, level of softening for each test fuel formulation, an implication that Fuel C is primarily responsible..

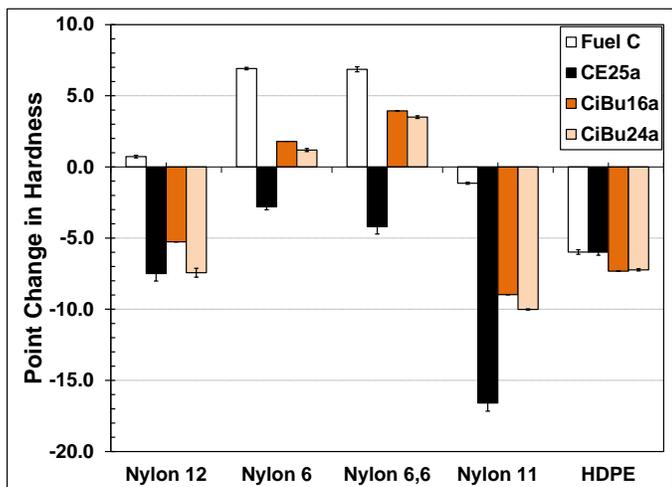


Figure 12. Point change in wet hardness results for the NBR specimens.

The nylons and HDPE showed slight changes in hardness following dry-out as shown in Figure 13. Interestingly, although the extent of hardness change was extremely low, it was consistent for both vapor and liquid exposures. Of the nylons evaluated in this study, the petroleum-based nylons showed a slight hardness increase with exposure to Fuel C. In contrast, the bio-based Nylon 11 exhibited a slight decrease. Of the petroleum-based nylons shown in Fig. 13, Nylon 12 showed a slight increase in hardness after being exposed to Fuel C and CE25a, while isobutanol did not change the hardness significantly from the baseline value. Nylons 6 and 6,6 showed a small increase in hardness with the exposure to Fuel C, but the hardness results were less affected by the addition of either ethanol or isobutanol. Nylon 11 showed the most sensitivity to the added alcohols. It was not significantly influenced by Fuel C, but CE25a and the isobutanol blends did result in a small level of softening. HDPE exhibited similar performance to either liquid or vapor exposure. Fuel C caused a slight decrease in the hardness, which was further softened (albeit) slightly by and ethanol and slightly more so by isobutanol.

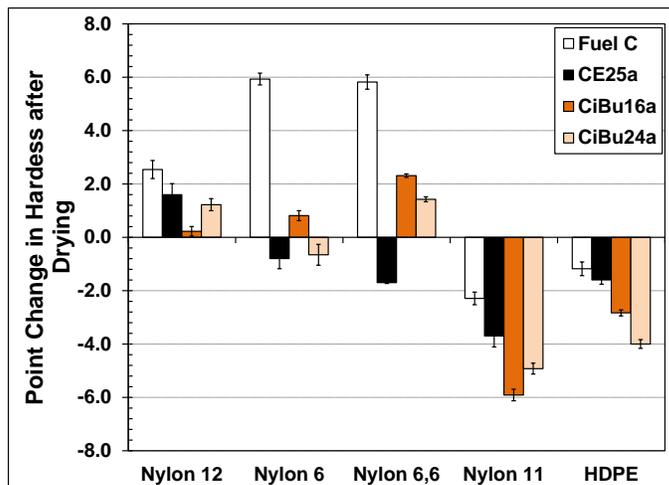


Figure 13. Point change in hardness results for the NBR specimens after drying at 60°C for 20 hours.

## Glass Transition Temperature Results

The glass transition temperature results for the four nylon materials and HDPE are shown in Figure 14. As shown in the figure, the  $T_g$  value for HDPE was relatively unaffected following exposure to the test fuels. However, the results for the nylons varied considerably with both fuel chemistry and type of nylon. The  $T_g$  value for Nylon 12 was raised around 20°C with exposure to Fuel C, while the addition of 25% aggressive ethanol had no appreciable effect. The test fuels containing isobutanol, on the other hand, did not appreciably affect  $T_g$  from the original baseline result. Both Nylon 6 and Nylon 6,6 exhibited similar shifts in  $T_g$  with exposure to the test fuels. For these two nylons, Fuel C produced a small to moderate increase in  $T_g$ , while the test fuels containing isobutanol had little additional effect. However, exposure to CE25a caused  $T_g$  to decline by 40°C and 60°C for Nylon 6 and Nylon 6,6, respectively. In contrast to the petroleum-derived nylons, Nylon 11 was unique in that the  $T_g$  value decreased, rather than increased with exposure to Fuel C; this drop in  $T_g$  was around 20°C from the original baseline value. CE25a caused  $T_g$  of Nylon 11 to decline an additional 15°C and exposure to the isobutanol fuel blends resulted in  $T_g$  decreasing approximately 60°C, from the baseline value. Nylon 11 was the plastic most affected by aggressive isobutanol.

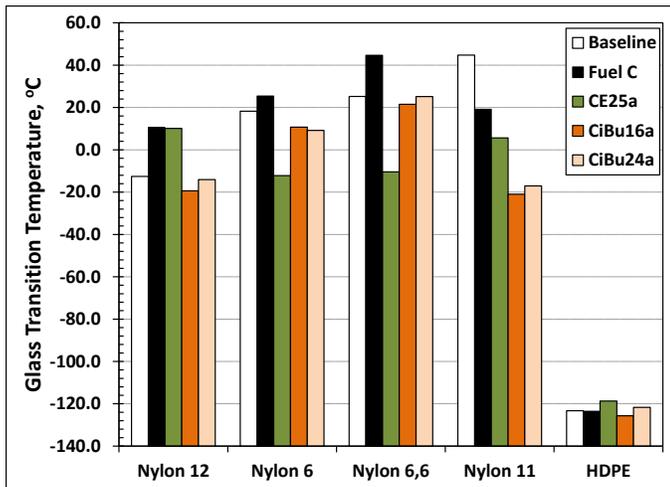


Figure 14. Glass transition temperature results for the NBR specimens after drying at 60°C for 20 hours.

### Other Common Plastics

#### Volume Change

In addition to the plastic types that were identified in fuel containment and storage systems, this study also included other common mid-range and commodity plastics. Their volume change following test fuel exposure is shown in Figure 15. The wet volume changes for the two acetals (POM and POM copolymer) and PBT were around 2 and 5%, respectively, and these results correspond to their predicted solubility. Fuel C increased the volume around 2.5% and an additional modest (2–3%) increase was observed when these specimens were exposed to the test fuels containing ethanol or isobutanol. In each case the measured volume swell for these materials was slightly higher with exposure to CE25a than for either CiBu16a or CiBu24a.

Moderate to high levels of swelling were observed for PP and PETG for each test fuel, and this result is consistent with the prior solubility analysis. For PP most, if not all, of this increase can be attributed to Fuel C, although isobutanol may add a small additional amount to the total volume. For PETG, Fuel C by itself increased the volume by 16%. The addition of either ethanol or isobutanol further increased the volume by another 7%, and there was no noticeable difference in the magnitude of swell resulting from CE25a, CiBu16a, or CiBu24a.

Interestingly, PTU reduced volume with exposure to CE25a, but CiBu16a and CiBu24a both produced a modest level of swelling (~5%), which was slightly higher than the level observed for Fuel C. Unlike ethanol, adding isobutanol to Fuel C did not cause a decrease in the volume. Rather a modest increase in swelling was observed for these fuel types.

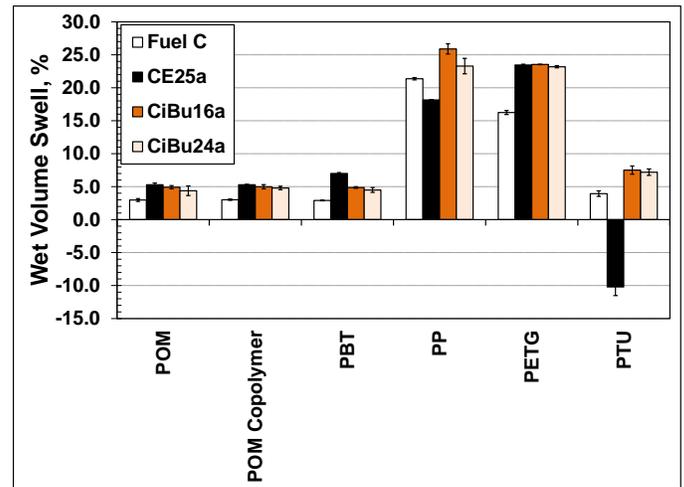


Figure 15. Wet volume swell results for other common plastics exposed to the test fuels for 16 weeks at 60°C.

As shown in Figure 16, the acetals (POM and POM copolymer) and PP exhibited only a slight increase in volume (over the baseline condition) following dry-out. PBT showed a small but significant gain in volume, while PETG experienced a large 10% increase. This increase is due to fluid retention, and appears to be stable and possibly permanent. The dried volume of PTU was not affected by Fuel C, but this material did exhibit a significant decrease volume when exposed to CE25a, CiBu16a and CiBu24a. (The dried volume for the PTU specimen exposed to CE25a was not made since this specimen had fractured.) The extent of the volume reduction following drying strongly indicates that PTU may not be considered compatible with the test fuels containing added ethanol or isobutanol.

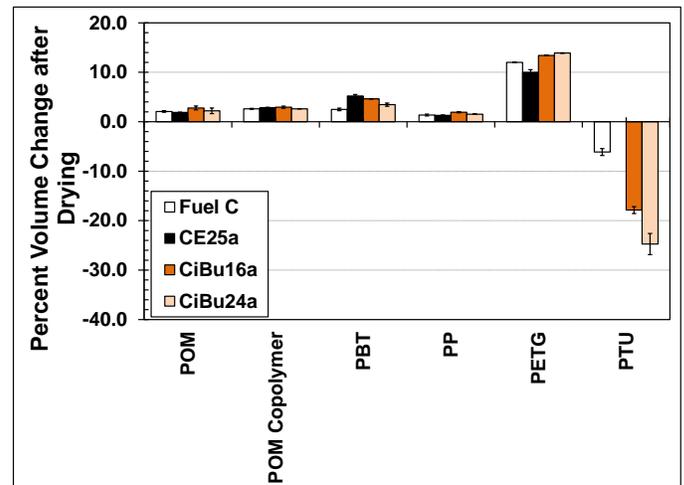


Figure 16. Volume change results for polyurethane, neoprene, SBR, and silicone after drying at 60°C for 20 hours.

#### Point Change in Hardness

The wetted hardness results for mid-range and commodity plastics are shown in Figure 17. POM and the POM copolymer both exhibited negligible softening with exposure to the test fuels containing one of the two types of alcohols. Fuel C did

not affect wetted hardness for POM. The hardness for PBT was lowered slightly by Fuel C, and the hardness dropped a total of 4–5 points for the test fuels containing either ethanol or isobutanol. This hardness decrease is considered small.

Polypropylene was observed to significantly soften with exposure to the test fuels. Its hardness was lowered by 13–15 points with exposures to the test fuels. Most of this drop in hardness is likely due to Fuel C, with little observable contribution from the alcohol additions. PETG is a mix of PET and an unknown co-polymer material. In contrast to PET (as shown in Figure 7), PETG was dramatically softened by the test fuels. Fuel C was responsible for a 15 point decrease in hardness (from baseline), and the added alcohols were observed to decrease hardness another 7–10 points. Clearly, the co-polymer had a significant (if not dominant) effect on the hardness result for this particular PET-based material.

As shown in the figure, PTU was the plastic most affected by the addition of alcohol. Fuel C did not affect PTU hardness significantly. However, ethanol and isobutanol reduced the hardness significantly by around 30 to 40 points. Of the two alcohol blended fuel types, CE25a decreased the hardness more than the isobutanol blends.

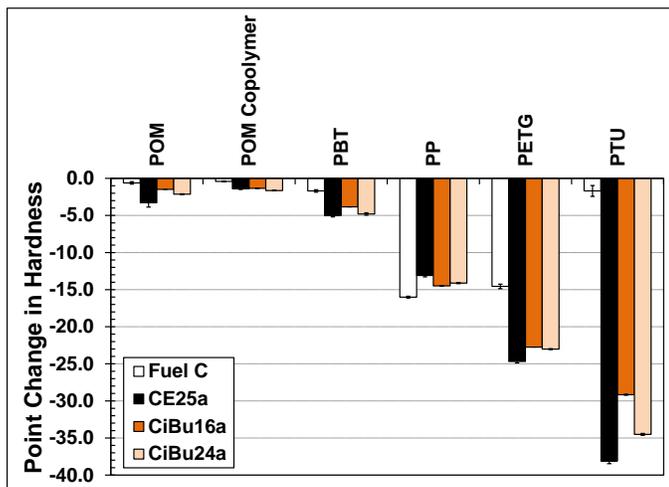


Figure 17. Point change in wet hardness results for common plastic specimens exposed to the test fuels for 16 weeks at 60°C.

The dried change in hardness results are shown in Figure 18. The change in hardness values for POM, POM copolymer, PBT and PP are considered negligible. However, small (but notable) softening occurred for PETG. This softening appears to be primarily caused by Fuel C for liquid exposures. In contrast to the other materials, the hardness for PTU was increased by exposure to the test fuels liquids, Fuel C has a noticeable effect, but CE25a caused additional embrittlement. CiBu16a and CiBu24a produced a smaller hardness increase than either Fuel C or CE25a.

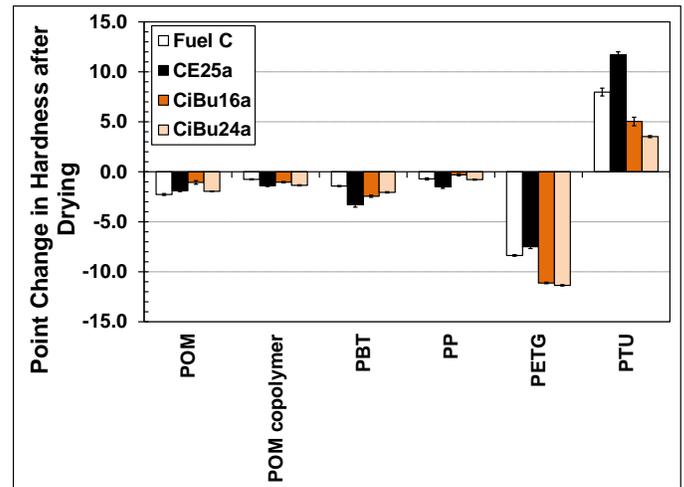


Figure 18. Point change in hardness results for other common plastic specimens after drying at 60°C for 65 hours.

### Transition Temperature

The glass transition temperature results for these plastic materials are shown in Figure 19. The two acetal plastic specimens, POM and the POM copolymer, did not undergo a shift in  $T_g$  following exposure to the test fuels. However, the specimens composed of PBT, PP, and PETG all exhibited significant declines in  $T_g$  accompanying exposure to Fuel C. PBT exhibited an additional 20°C decline in  $T_g$  when exposed to CE25a, and an additional 15°C reduction for the test fuels containing isobutanol.

PP and PETG did not show any added effect when either alcohol type was added to the Fuel C formulation, indicating that Fuel C was primarily responsible for the observed downward shift. PTU exhibited a small decline in  $T_g$  with Fuel C exposure, but the isobutanol was observed to produce a small increase in  $T_g$  (from baseline). PTU was not exposed to CE25a, so no data are available.

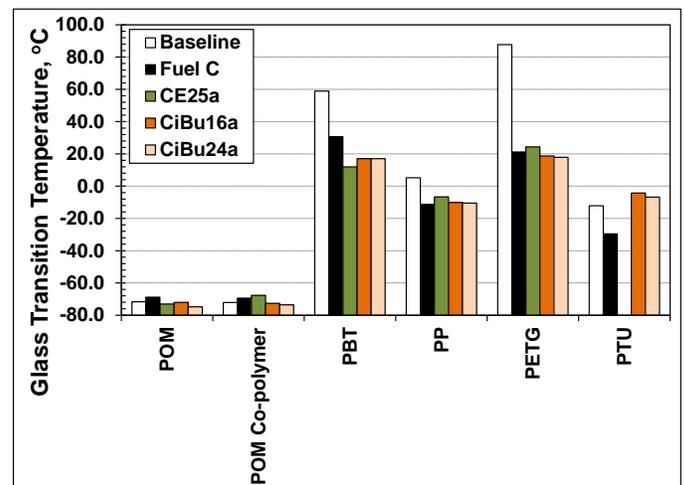


Figure 19. Glass transition temperature results for other common plastic materials after drying at 60°C for 65 hours.

## Fiberglass Resins

### Volume Change

The results for the vinyl ester (Vipel F085) and terephthalic polyester (Vipel F774) resins are shown together in Figure 20. For both materials, the volume increases were similar. Two isophthalic polyester resins were also tested but, although they were intact following exposure to Fuel C, they had partially dissolved and fractured with exposure to CE25a, CiBu16a, or CiBu24a, and therefore are not included in the results. Solubility analysis predicted low to moderate swelling for these two materials, and that the vinyl ester resin would have better compatibility to the test fuels than the terephthalic resin. The results show reasonable correlation with the predicted solubility. However, the vinyl ester resin showed considerably higher swell with CE25a than with Fuel C or fuels containing isobutanol.

The swelling results for the vinyl ester resin correlate well with the solubility curve for Fuel C and the isobutanol test fuels. The vinyl ester resin showed negligible volume swell with Fuel C, and low swell (5%) with the isobutanol test fuels. However, this resin type was highly sensitive to ethanol as shown by the 22% volume expansion accompanying CE25a exposure. The terephthalic ester resin swelled 7% with Fuel C, while the alcohol additions pushed the volume swell to between 24 and 26%. Unlike vinyl ester, the added isobutanol did not show improved compatibility over CE25a.

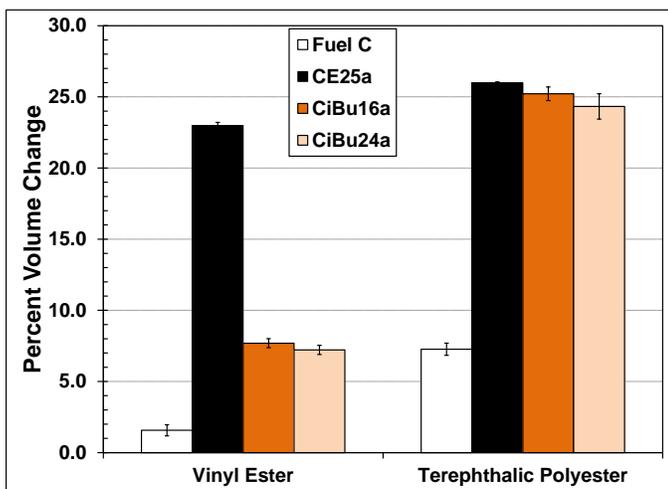


Figure 20. Wet volume swell results for the fiberglass resins. Specimens were submerged in the test fuels for 16 weeks at 60°C.

The volume change for the two fiberglass resins after drying was significant, as shown in Figure 21. The terephthalic polyester resin dried volume was 5% higher than the starting condition following exposure to Fuel C. The addition of 25% ethanol and 24% isobutanol increased the dried volume to around 12 and 17%, respectively. After drying, the vinyl ester resin returned near the original condition when exposed to Fuel C. The addition of 25% ethanol had a pronounced effect by raising the dried mass by 10% and the starting volume by 13%. For this resin material, isobutanol increased the volume to around 5%, which roughly matches the swell observed for terephthalic polyester resin exposed to Fuel C. The observed

increase in mass and volume indicate retention of test fuels (or one of their components) in the plastic structure.

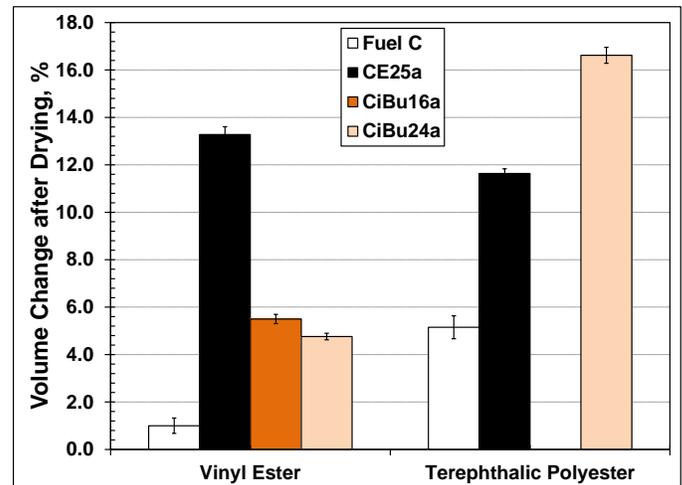


Figure 21. Volume change results for the fiberglass resins after drying at 60°C for 65 hours.

### Point Change in Hardness

The results for the two fiberglass resins, following immersion in the test fuels, are presented in Figure 22. Both resin types experienced hardness reductions in proportion to their level of volume swell. Softening for the vinyl polyester was essentially negligible with Fuel C and the isobutanol test fuels, but a significant hardness decrease occurred with exposure to CE25a. The terephthalic ester resin was slightly softened by Fuel C, but the alcohol additions significantly added to the level of observed softening.

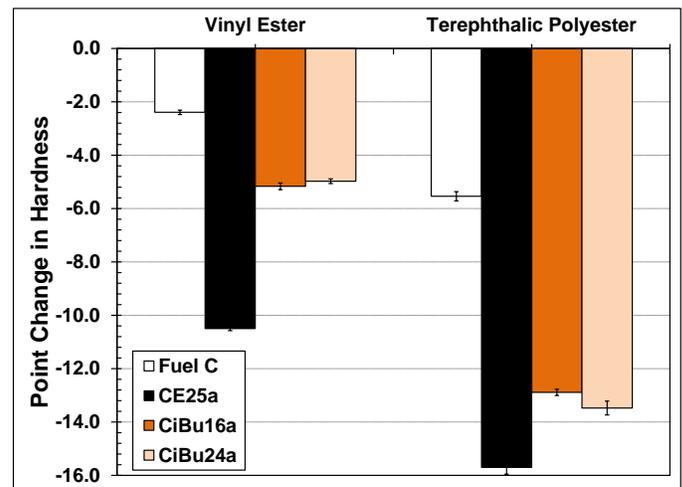


Figure 22. Point change in wet hardness results for fiberglass resin specimens exposed to the test fuels for 16 weeks at 60°C.

The dry-out hardness results for the two resins which survived fuel exposure are shown in Figure 23. The surviving resins remained in a slightly softened state after drying and the vinyl ester was observed to soften the least amount. The terephthalic polyester resin showed a small drop in hardness with exposure to Fuel C, CE25a produced a slightly higher

drop in hardness and the isobutanol blended fuels caused the hardness to drop by 7–8 points. For each resin the Fuel C vapors did not affect the dried hardness, but they were softened by a small amount when exposed to CiBu16a and CiBu24a.

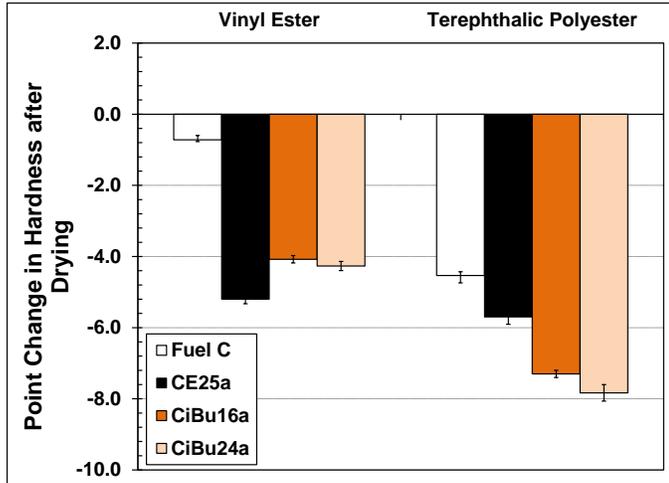


Figure 23. Point change in hardness results for fiberglass resin specimens after drying at 60°C for 65 hours.

### Transition Temperature

The glass transition temperature results for the two resin materials are presented in Figure 24 and show that these two resins behave somewhat differently when exposed to the test fuels. Terephthalic polyester undergoes a 40°C drop in  $T_g$  with exposure to Fuel C, while  $T_g$  for vinyl ester is unaffected. The addition of 25% aggressive ethanol to Fuel C significantly lowered the value of  $T_g$  for the vinyl ester resin, but had only small effect (beyond Fuel C) for the terephthalic polyester sample. The test fuels containing isobutanol significantly lowered  $T_g$  for both materials, but for the vinyl ester the effect was less pronounced than for CE25a. The terephthalic polyester, on the other hand, exhibited the greatest decline in  $T_g$  with the isobutanol additions. Unfortunately, no CE25a exposures were performed in the vapor-phase region for comparison.

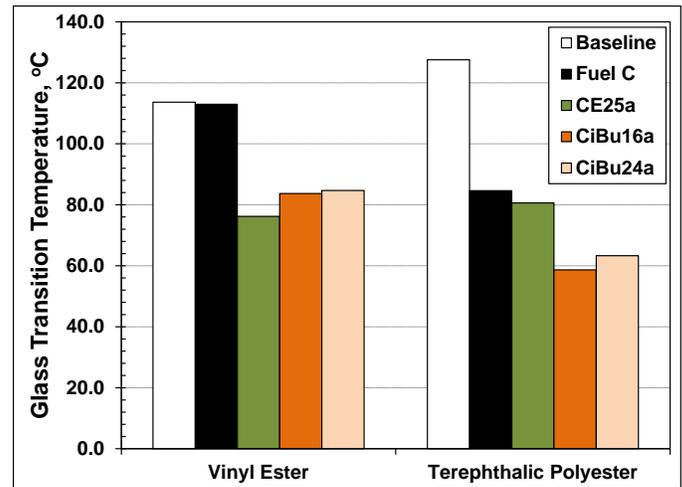


Figure 24. Glass transition temperature results for fiberglass resin specimens after drying at 60°C for 65 hours.

### Discussion

In general the level of swell was much lower for plastic materials than was observed for elastomers. This observation is not surprising since, for many of the plastic materials in this study, the predicted solubility was much lower than that of the elastomers. However, for several materials, such as PVDF and nylon, the solubility analysis indicated that these materials should be relatively insoluble to the test fuels, but this was not the case. Likewise the measured volume swell for the resins was higher than would be expected from the solubility analysis. The reason for this discrepancy is attributed to the Hansen solubility parameters. The HSP values for these materials were selected from literature sources and, as a result, may not accurately represent the plastic grades used in this study.

The resins evaluated in this study represent grades used in fiberglass piping and underground storage tanks. It is important to note that these coupons consisted of pure resin only. In practice these resins are combined with fiberglass, and their role is to bind the fibers in a matrix. The glass fibers, by themselves, are not reactive and they would serve not only as a barrier to fuel penetration, but their high strength and inelasticity, would cause the composite structure to resist swelling.

### Summary/Conclusions

In spite of some notable exceptions, the Hansen solubility method generally provided good to excellent agreement to the observed volume swell for many of the plastic materials. The plastics that exhibited the lowest volume swelling (and smallest change in hardness) in the test fuels were the permeation barrier materials: PPS, PET, PVDF, and PTFE.

The performance of the nylons was varied. Nylon 6 and 6,6 showed negligible swell with Fuel C and the isobutanol test fuel, but swelled to around 5% in CE25a. Nylon 11, which is made from vegetable oil, expanded 5% in Fuel C, 18% in CE25a, and around 15% in the test fuels containing isobutanol. HDPE underwent a modest and consistent amount of swell

following exposure to the test fuels; the added alcohols did not appear to have an effect.

The acetals (POM and POM co-polymer) and PBT exhibited modest (~5%) swelling and softening with exposure to the test fuels. The presence of ethanol or isobutanol in the test fuel had little additional effect for the acetals. However, for PBT, Fuel C lowered the transition temperature by 30°C, and this value declined another 10 degrees for the test fuels containing isobutanol or ethanol. PP swelled to 20% and higher with exposure to the test fuels. Most of this increase was due to Fuel C, but isobutanol did produce a small additional increase. PP was also significantly softened by the test fuels when wetted but otherwise was not affected by the test fuels. The swelling and softening results observed for PETG were similar to PP, except that the transition temperature was lowered 70°C by the test fuels. This dramatic drop in temperature is a strong indicator that the test fuels (primarily Fuel C) significantly altered the molecular structure of the material. Of the plastics investigated in this study, PTU was the material most impacted by the adding of alcohol, especially ethanol. The volume increased modestly with exposure to Fuel C, CiBu16a, and CiBu24a, but CE25a caused PTU to lose ~10% volume and mass.

Four fiberglass resins were tested and all were found to be sensitive to alcohol blends. Only two of the four resins (terephthalic polyester and vinyl ester) remained intact following exposure to CE25a, CiBu16a, and CiBu24a. (The two isophthalic polyesters and the epoxy resins fractured during the exposure runs and are not viewed as compatible with gasoline-alcohol fuels.) Terephthalic polyester swelled around 7% with Fuel C, but swelling increased to around 25% for the fuels containing either ethanol or isobutanol. The vinyl ester resin performed much better, as it exhibited modest swelling (5%) when exposed to the test fuels containing isobutanol. When exposed to CE25a, the vinyl ester resin specimens swelled 23%. These resins were also significantly softened by CE25a, but the other test fuels only modestly impacted the hardness. In the dried state, these resins remained slightly softened, and more significantly the glass-to-rubber transition temperatures dropped 30°C or more with the fuel formations containing ethanol or isobutanol. Large declines in glass-to-rubber transition temperature are indicative of structural changes in the resins.

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## Definitions/Abbreviations

<b>ASTM</b>	American Society for Testing and Materials	<b>IR</b>	interaction radius
<b>CiBu16a</b>	test fuel composed of 84% Fuel C and 16% aggressive isobutanol	<b>ORNL</b>	Oak Ridge National Laboratory
<b>CiBu24a</b>	test fuel composed of 76% Fuel C and 24% aggressive isobutanol	<b>PBT</b>	polybutylene terephthalate
<b>CE25a</b>	test fuel composed of 75% Fuel C and 25% aggressive ethanol	<b>PET</b>	polyethylene terephthalate
<b>d<sub>s</sub></b>	solubility distance	<b>PETG</b>	PET copolymer
<b>DMA</b>	dynamic mechanical analysis	<b>POM</b>	polyoxymethylene
<b>DOE</b>	US Department of Energy	<b>PP</b>	polypropylene
<b>E10</b>	gasoline containing 10% ethanol	<b>PPS</b>	polyphenylene sulfide
<b>E15</b>	gasoline containing 15% ethanol	<b>PTU</b>	polythiourea
<b>EPA</b>	US Environmental Protection Agency	<b>PVDF</b>	polyvinylidene fluoride
<b>FRP</b>	fiber-reinforced plastic	<b>SAE</b>	Society of Automotive Engineers
<b>Fuel C</b>	test fuel composed of 50% isooctane and 50% toluene	<b>T<sub>g</sub></b>	glass transition temperature
<b>HDPE</b>	high density polyethylene		
<b>HSP</b>	Hansen solubility parameter		

