

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

Michael D. Kass, Chris Janke, and Timothy Theiss
Oak Ridge National Laboratory

James Baustian and Leslie Wolf
Butamax Advanced Biofuels LLC

Wolf Koch
Technology Resources International

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 to 15% 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.

CITATION: Kass, M., Janke, C., Theiss, T., Baustian, J. et al., "Compatibility Assessment of Plastic Infrastructure Materials with Test Fuels Representing E10 and iBu16," *SAE Int. J. Fuels Lubr.* 8(1):2015, doi:10.4271/2015-01-0894.

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.

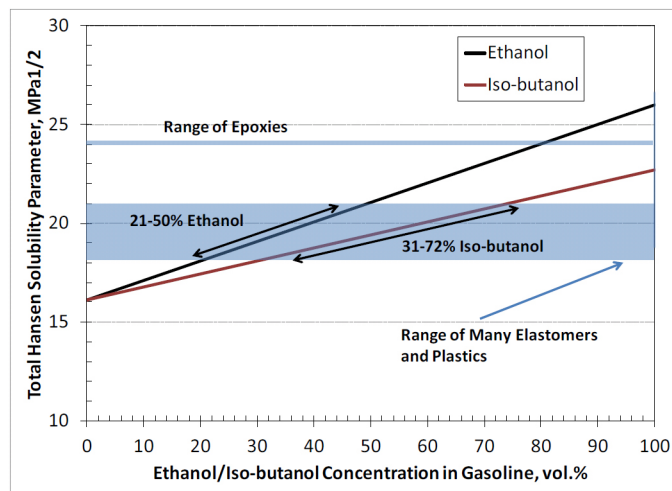


Figure 1. Total solubility parameter curves for gasoline blended with ethanol or isobutanol.

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 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.

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.

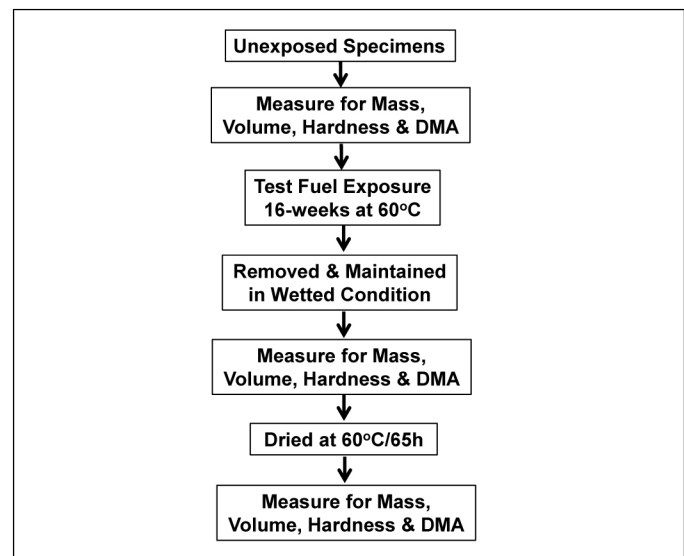


Figure 2. Flow chart showing the exposure protocol and test methods.

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