

Compatibility Assessment of Elastomer Materials to Test Fuels Representing Gasoline Blends Containing Ethanol and Isobutanol

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ABSTRACT

The compatibility of elastomeric materials used in fuel storage and dispensing applications was determined for test fuels representing neat gasoline and gasoline blends containing 10 and 17 vol.% ethanol, and 16 and 24 vol.% isobutanol. The actual test fuel chemistries were based on the aggressive formulations described in SAE J1681 for oxygenated gasoline. Elastomer specimens of fluorocarbon, fluorosilicone, acrylonitrile rubber (NBR), polyurethane, neoprene, styrene butadiene rubber (SBR) and silicone were exposed to the test fuels for 4 weeks at 60°C. After measuring the wetted volume and hardness, the specimens were dried for 20 hours at 60°C and then remeasured for volume and hardness. Dynamic mechanical analysis (DMA) was also performed to determine the glass transition temperature (T_g).

Comparison to the original values showed that all elastomer materials experienced volume expansion and softening when wetted by the test fuels. The fluorocarbons underwent the least amount of swelling (<25 %) while the SBR and silicone samples exhibited the highest level of expansion (>100%). The level of swelling for each elastomer was higher for the test fuels containing the alcohol additions. In general, ethanol produced slightly higher swell than the oxygen equivalent level of isobutanol. When dried, the fluorocarbon specimens were slightly swollen (relative to the baseline values) due to fuel retention. The NBRs and neoprene exhibited shrinkage and embrittlement associated with the extraction of plasticizers. SBR also experienced shrinkage (after drying) but its hardness returned to the baseline value. The dried volumes (and hardness values) of the silicone, SBR and fluorosilicone rubbers closely matched their original values, but the polyurethane specimen showed degradation with exposure to the test fuels containing ethanol or isobutanol. The DMA results showed that the test fuels effectively decreased T_g for the fluorocarbons, but increased T_g for the NBR materials. The T_g values other elastomers were not affected by the test fuels.

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INTRODUCTION

Renewable fuels are becoming more widely used as 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 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.² 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 EPA approved a waiver to allow the use of 15% ethanol in gasoline (E15).³ However, concerns were raised that as the ethanol concentration in gasoline is increased, the fuel may become less compatible with the

existing fueling infrastructure, a significant portion of which was originally designed for E0 use. 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.^{4,5} Elastomeric materials need to be considered since they are used extensively in fuel lines as hoses and as seals. Their performance, when exposed to a particular solvent, is critical to ensure leak-tight joining of structural components and proper operation of valves, meters and sensors. Failure of a seal 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 elastomers when they are exposed to new gasoline fuels, such as those containing oxygenates. Data, provided from controlled compatibility experiments, better enables proper seal selection, and can help identify those sites in fueling hardware systems susceptible to leakage.

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.⁶ Isobutanol is of interest since it has a higher energy density relative to ethanol. It is also less volatile and less water soluble.

The focus of this investigation was to develop a data set of properties (relevant to compatibility) for elastomers exposed to gasoline blends of ethanol and isobutanol. The test fuels included a gasoline standard, and blends containing 10 and 17% ethanol, and 16 and 24% isobutanol. (Gasoline blends containing 16 and 24% isobutanol have the oxygen equivalent amounts of E10 and E15, respectively.) 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 to determine if the Hansen solubility method can effectively predict relative swelling for each material and test fuel. The elastomer types evaluated in this study included those common to fueling infrastructure systems. This list included fluorocarbons, fluorosilicone, acrylonitrile rubbers (NBRs), neoprene, polyurethane, styrene butadiene, and silicone rubber. Data obtained from the prior ethanol compatibility studies on these materials are included for additional interpretation and summary.

SOLUBILITY AND ITS IMPACT ON OTHER ELASTOMER PROPERTIES

For polymers, such as elastomers, fuel compatibility is predominantly determined by the mutual solubility between the elastomer 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

using the Hansen solubility approach, which is based on Flory-Huggins solubility theory.⁷ The Hansen solubility approach separates out the solubility contributions according to dispersion, dipole and hydrogen bonding forces. For illustrative purposes it is often useful to combine these parameters into a single parameter, known as the total Hansen solubility parameter.

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 parameter of gasoline blended with ethanol or isobutanol increases with alcohol content. Also depicted in the figure is the typical range of total solubility parameters for many elastomers. As the total solubility parameter of the fuel approaches the values for elastomers and plastics, the potential for higher solubility, and hence polymer swelling, is increased. For ethanol concentrations between 15% and 49%, high solubility, and therefore peak swell, is predicted for many elastomers. Another consideration is that elastomers 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 evaluated by solubility parameter theory.

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 polymers and test fuels evaluated in this study are 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.

Elastomers are a class of polymers which are predominantly used in sealing applications. Large o-ring and seal manufacturers, such as Parker and Dichtomatic, provide compatibility tables of their products with various solvents including ethanol, toluene and isooctane.^{8,9} These tables rank compatibility performance solely on the level of volume swell measured for a particular solvent.

For seal applications, shrinkage of the elastomer upon drying is also a critical parameter since a contraction of volume can conceivably enable leakage to occur. Shrinkage is also indicative of the removal of one or more components of the elastomers (by the solvent). This extraction of additives can negatively change the properties of the elastomer, leading to reduced performance and durability. For most seal applications, some level of volume swell is acceptable, since the expansion will serve to maintain the seal. The actual acceptable level of swell is dependent on the particular

application. It is known that excessive swell can lead to extrusion of the elastomer beyond the sealed interface where it becomes susceptible to damage. Also, since high swell is indicative of high solubility, there is a heightened potential for fluid to permeate through the seal material and into the environment. The absorption of fluid into the elastomer is typically accompanied by a reduction in its hardness, since the added fluid lowers its resistance to penetration.

The change in hardness following drying is another key property used to assess whether structural or compositional changes have taken place in the elastomer from the exposure to the test fuels. An elastomer, which was not compounded with plasticizers, would not typically be accompanied by a change in hardness (unless the polymer chemically reacted with the test fuel). Plasticizers, such as phthalates, are often added to impart pliability (or softness) to an otherwise brittle material. If a solvent was able to extract the plasticizer from the elastomer structure, then the volume (after drying) would decrease due to the reduction in overall mass. The hardness would be expected to increase since the softening component has been removed. Shrinkage accompanied by a loss in hardness is indicative of chemical degradation of the polymer.

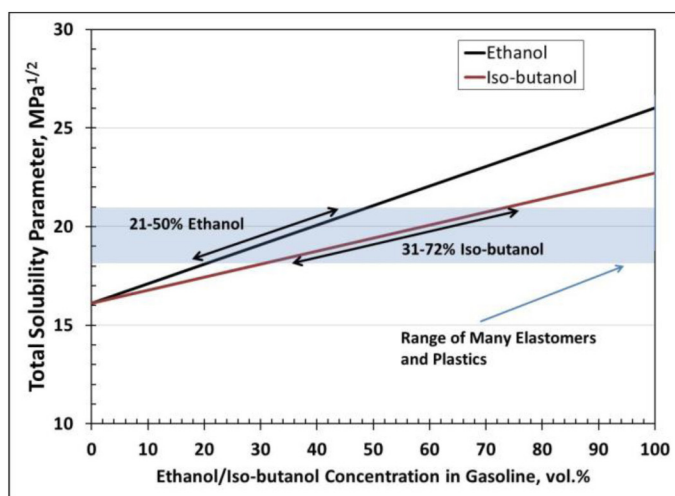


Figure 1. Total solubility parameter curves for gasoline blended with ethanol or isobutanol.

MATERIALS, EQUIPMENT AND PROCEDURE

Test Fuels

In this study test fuels representing gasoline, and gasoline blended with 10% and 17% ethanol were prepared along with blends containing 16% and 24% isobutanol. These fuels, denoted as Fuel C, CE10a, CE17a, CiBu16a and CiBu24a, were based on the aggressive standards described in SAE J1681.¹⁰ Fuel C is a 50:50 blend of isooctane and toluene and is representative of high aromatic grades of gasoline. The aggressive ethanol formulation followed the one outlined in SAE J1681; however, this standard does not include butanol (isomers). The CE17a test fuel contains 17% ethanol, but was

selected to represent E15 to account for the possibility that the actual ethanol content in gasoline may, in fact, vary by several percentage points. The CE17a fuel formulation also matches the one used in a corresponding investigation by Underwriters Laboratories.¹¹

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. Completely 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 ASTM International (formerly referred to as the American Society for Testing and Materials). 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. 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. (Units are in grams.)

Component	Aggressive Ethanol	Aggressive Isobutanol
CDA Ethanol	781.6	-----
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

Elastomer Materials

The elastomer materials evaluated in this study included two fluorocarbons (Viton A401C and Viton B601), six NBRs and one type of fluorosilicone, polyurethane, neoprene, SBR, and silicone. The NBR grades include those developed for use as fuel lines or hoses, while the other elastomers were selected as generic representatives, and therefore may not represent actual grades used in fueling systems. Three specimens were evaluated for each elastomer type, and the length, width, and thickness for each were 3.8, 1.3, and 0.2 cm (1.5, 0.5, and 0.08 in.), respectively.

Experimental Protocol

Much of the experimental protocol was determined from an earlier study which found that full saturation of the elastomers was achieved following a 4-week exposure period.⁴ A test temperature of 60°C was selected to be consistent with the dispenser test protocol used by Underwriters Laboratories.¹¹ 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 4 weeks (after which they were fully saturated), then they were removed and measured for volume, mass, and Shore A hardness while in the wetted (or saturated) state. The hardness measurements were performed individually on each specimen and were found to match the hardness values provided by the suppliers. (The specimens were not doubled up to achieve the desired Shore A test thickness of 0.635 cm.) Once the wetted properties were measured, the elastomers were heated at 60°C for 20 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.

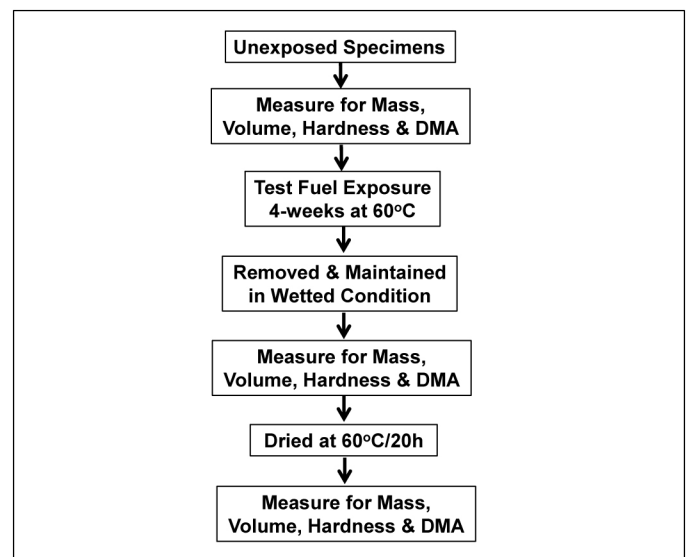


Figure 2. Flow chart showing the exposure protocol and test methods.

Dynamic mechanical analysis (DMA) testing was also performed to further evaluate whether any structural changes had taken place in the polymers following exposure.¹² 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. 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 transitions to a more pliable rubbery state. The temperature associated with this onset is the glass transition temperature, T_g . The ability to flex and deform is