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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.

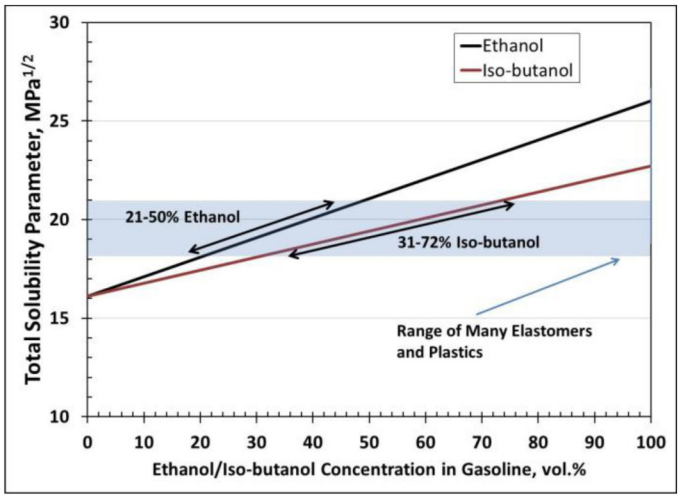

Figure 1. Total solubility parameter curves for gasoline blended with ethanol or isobutanol.

MATERIALS, EQUIPMENT AND PROCEDURE

Test Fuels

In this study test fuels representing gasoline, and gasoline blended with10% 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 Reagent grade isobutanol	781.6 --------	------- 797.7
De-ionized water	8.103	7.987
Sodium chloride	0.004	0.004
Sulfuric acid	0.021	0.021
Glacial acetic acid Isobutyric acid	0.061 -------	------- 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.

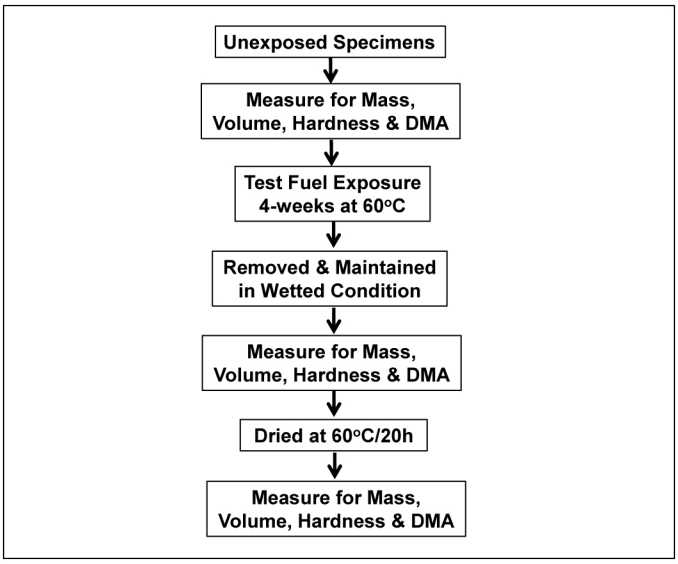

Figure 2. Flow chart showing the exposure protocol and test methods.

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 known as the glass transition temperature, T_g. The ability to flex and deform is

important in most sealing applications and the operational range of elastomers is bounded by the temperatures associated with T_g and the melting point. 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 increased, then the operational range of the elastomer decreases as well and the possibility exists (depending on the value) that the seal will behave in a brittle manner instead of the more pliable one it was originally designed for.

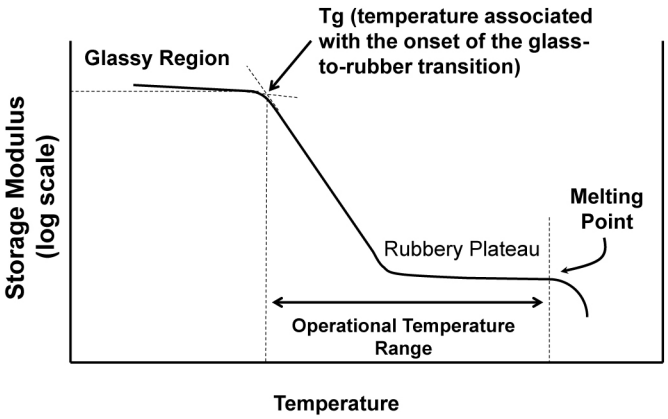

Figure 3. Representative DMA results for a polymer material.

RESULTS

Solubility Analysis

A solubility analysis was performed for the elastomer materials with fuel blends representing gasoline (Fuel C), E10, iBu16, E15, and iBu24. The analytical approach was based on the Flory-Huggins model using the Hansen solubility parameter (HSP) methodology.7 This type of analysis is useful in predicting swelling behavior in polymeric materials exposed to known solvents. 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 low to moderate swelling is expected for the fluoroelastomers and polyurethane, while moderate to high swelling is expected for NBRs, neoprene, and SBR. The highest level of volume swell is predicted for silicone. Ranking these materials in order of predicted extent of swell yields silicone>SBR>NBR> neoprene>fluoroelastomers >polyurethane. This solubility analysis also indicates that (in general) higher swelling should be observed for the test fuels containing the added alcohols, and that CE10a and CE17a may produce more swelling that the oxygen equivalent iCBu16 and iCBu24 test fuels.

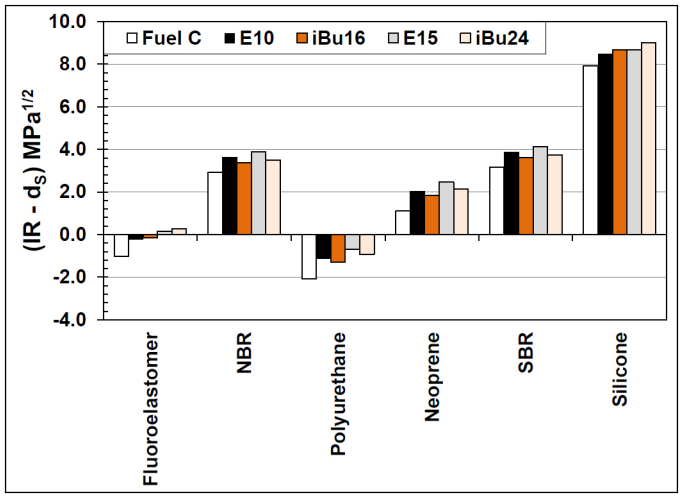

Figure 4. Solubility analysis results for the elastomer materials.

Mass and Volume Change

The resulting changes in mass for each elastomer type were found to be nearly identical to the corresponding changes in volume. Since volume change is the property most commonly used in assessing polymer compatibility, and since the mass change was essentially equivalent to the volume change, the mass change results were not included in this paper.

Fluoroelastomers

Volume Change

The fluoroelastomer materials in this study included two fluorocarbon specimens and one fluorosilicone specimen. The results for the volume change (from baseline) in the wetted and dried conditions are shown in Figures 5 and 6, respectively.

All of the fluoroelastomer specimens swelled with exposure to Fuel C and additional swell was noted with the test fuels containing ethanol or isobutanol. For the two fluorocarbons, the volume swelled between 12 and 15%, while the fluorosilicone specimen expanded by 20%. It is important to note that fluorosilicone is a mixture of both fluorocarbon and silicone rubber and the silicone fraction would be expected to produce a higher volume swell than a straight fluorocarbon. The addition of 10% aggressive ethanol was observed to further increase the volume by another 5% for the fluorocarbons, but only caused a small 2% increase with the fluorosilicone. Increasing the ethanol content to 17% resulted in a slightly higher increase in volume for the fluorocarbons, but no additional increase was observed for the fluorosilicone.

The addition of 16 and 24% aggressive isobutanol produced additional volume change over the Fuel C baseline for the two fluorocarbons but at a level equal to or less than that achieved

from the ethanol exposures. For the fluorosilicone specimen, isobutanol was observed to produce a slightly lower volume swell than Fuel C. Isobutanol concentration had little, if any, effect on the volume.

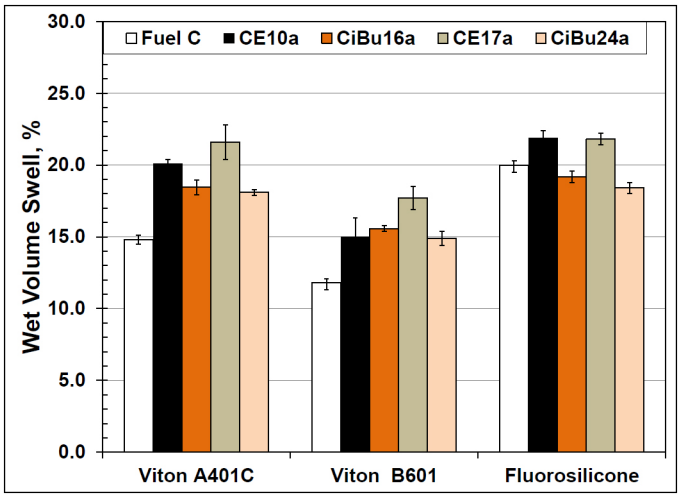

Figure 5. Wet volume swell results for the fluoroelastomer specimens.

The volume change for the two fluorocarbons and fluorosilicone specimen following dry-out is shown in Figure 6. For the two fluorocarbons, the extent of volume swell was similar to that of the wetted specimens (Figure 5), indicating that the test fuel liquid was not completely removed by drying. This effect was also noted by other researchers.13 Fuel C was a primary contributor to this retained volume and, interestingly, the volume swell was lower for CE10a and CE17a, respectively.

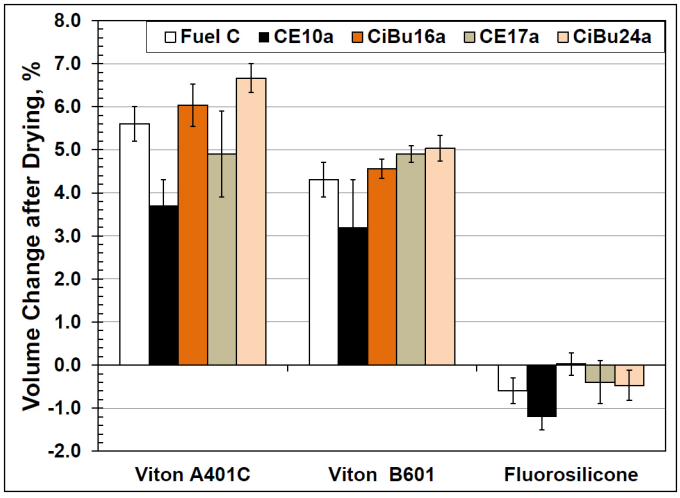

Figure 6. Volume change results for the fluoroelastomer specimens after drying at 60°C for 20 hours.

The resulting retained volume expansion varied slightly with ethanol concentration for the two fluorocarbons. Viton A401C exhibited a slightly lower dried volume for the ethanol fuel blends. For Viton B601, the dry-out volume associated with CE10a was slightly less than that achieved for Fuel C, while that with CE17a was slightly higher. The addition of isobutanol slightly increased the dry-out volume, and this effect is attributed to the larger molecular size of isobutanol (relative to ethanol) and, possibly, the lower vapor pressure of isobutanol. The larger molecule size means than isobutanol would be less mobile (and therefore less diffusive) in the polymer structure than ethanol at a given temperature.

Point Change in Hardness

The wet hardness results for the three fluoroelastomer materials are shown in Figure 7. The two fluorocarbons exhibited similar declines in hardness (from the baseline condition). The added ethanol and isobutanol resulted in an additional 3 to 5 point decrease in hardness (which is quite low relative to the absolute baseline hardness value). In general the aggressive isobutanol additions did not produce as much softening as did the fuel formulations containing aggressive ethanol. The fluorosilicone specimen exhibited more decline in hardness than the fluorocarbons, but these values (especially when compared to Fuel C) are not considered noteworthy.

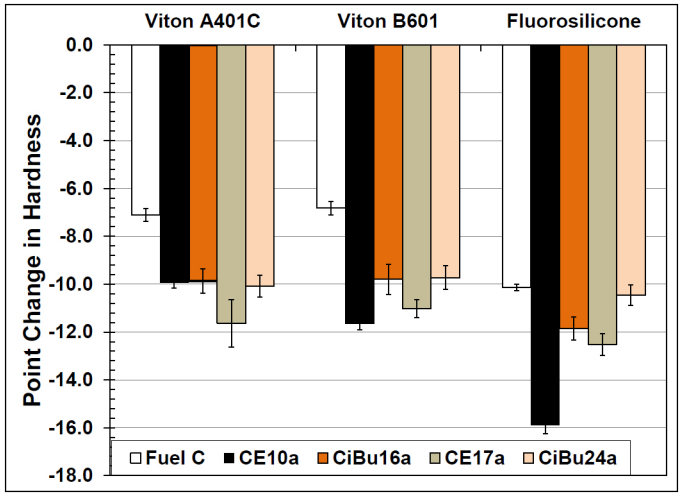

Figure 7. Point change in wet hardness results for the fluoroelastomer specimens.

The dry-out hardness results (Figure 8) for the three fluoroelastomers showed that these materials remained in a slightly softened state following drying. The two fluorocarbons show a slight 2 to 3 point decrease in hardness (softening) upon exposure to Fuel C and an additional 3 points for the test fuels containing aggressive ethanol and aggressive isobutanol. The test fuels containing isobutanol produced a slightly higher softening (hardness decline) than does ethanol, and this added effect is attributed to the increased retention of isobutanol in the dried specimens as indicated previously in Figure 7. The fluorosilicone specimen was relatively unaffected by the test fuels; a 2 point drop in hardness was noted for the fuels containing ethanol and isobutanol, but this number is probably too low to be considered significant.

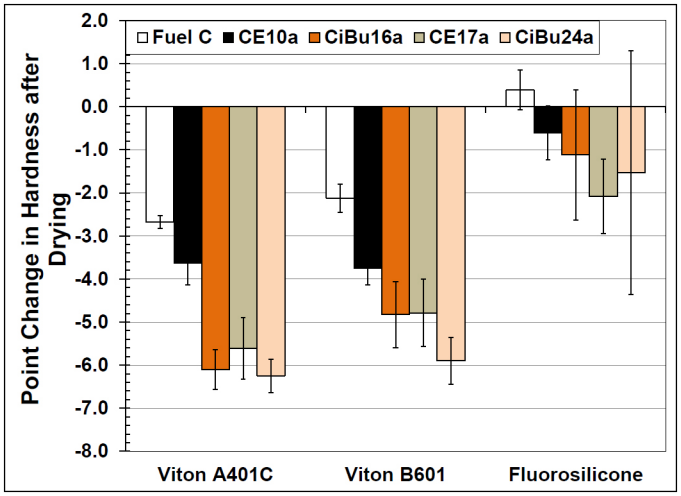

Figure 8. Point change in hardness results for the fluoroelastomer specimens after drying at 60°C for 20 hours.

Transition Temperature

As shown in Figure 9, the two fluorocarbons (Viton A401C and Viton B601C) both exhibited a decrease in glass transition temperature with exposure to the test fuels. The primary cause for this downward shift was Fuel C, as the additions of aggressive ethanol or aggressive isobutanol do not appear to have any additional impact on T_g beyond that observed for Fuel C. This reduction in the glass transition temperature is associated with the retention of the test fuel liquid in the fluoroelastomer structure and the resulting expansion in volume. This volume increase allows molecular relaxation to occur at lower temperatures than unexposed elastomers. For fluorosilicone, the glass transition temperature appeared to be unaffected when exposed to the test fuels.

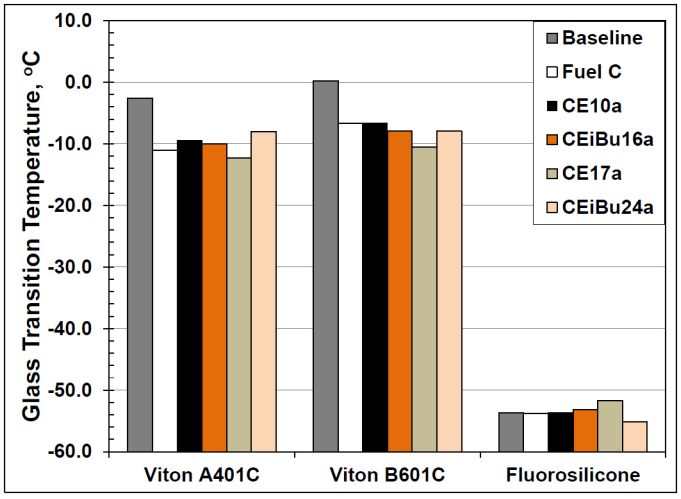

Figure 9. Glass transition temperature results for the fluoroelastomer specimens after drying at 60°C for 20 hours.

Acrylonitrile Rubbers

Volume Change

The volume change results for the six nitrile rubbers are shown in Figure 10. Although there is some variability according to rubber type, the relative volume swelling for test fuels containing ethanol and isobutanol was in agreement with the solubility analysis performed in Figure 4. In general the specimens swelled between 17 and 25% with exposure to Fuel C (depending on the type). Exposure to 10% aggressive ethanol increased the volume swell considerably, although raising the ethanol content to 17% produced only a small additional expansion. The volume expansion associated with oxygen equivalent levels of isobutanol was either the same or slightly less than that achieved with equivalent ethanol. Interestingly, the volume swell for all NBRs was observed to increase with increased ethanol content, whereas the volume swell was essentially unchanged between 16 and 24% isobutanol. This observation was also noted for the fluoroelastomers.

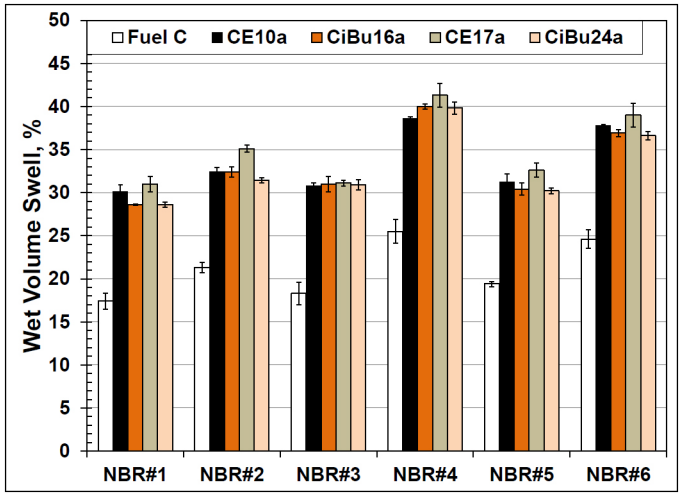

Figure 10. Wet volume swell results for the six NBR specimens.

All of the NBRs underwent significant volume contraction (between 10 and 18%) following dry-out as shown in Figure 11. All of the specimens, except NBR#3, which was a marine grade, shrank between 13 and 18%. The results suggest that Fuel C is the component most responsible for this contraction, although ethanol had a minor additional contribution for NBR#1 and NBR#4. The specimens exposed to the test fuels containing isobutanol exhibited a similar volume contraction as those exposed to Fuel C. This result suggests that isobutanol has an insignificant effect on the overall shrinkage for these materials. The removal of a significant amount of NBR mass and volume indicates that dissolution and extraction of one or more components had occurred. The volume reduction for the marine-grade NBR was around 10%, which was measurably lower than that of the other NBRs. The other NBR grades were found to exhibit similar performance in volume reduction for each test fuel.

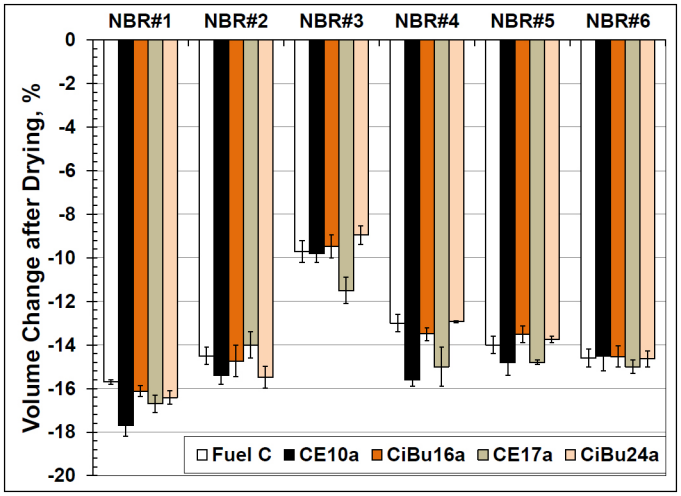

Figure 11. Volume change results for the six NBR specimens after drying at 60°C for 20 hours.

Point Change in Hardness Results for Wet and Dry Conditions

Except for the fluoroelastomers, the NBR specimens (as a group) showed the lowest drop in wet hardness from the baseline condition. The behaviors for the different NBR specimens were similar to each other as shown in Figure 12, although the marine grade (NBR#3) exhibited significantly less softening than the other types. The NBRs (excluding NBR#3) declined 15 to 20 points with exposure to Fuel C in the wetted state, while NBR#3 declined by 10 points. This drop in hardness is significant relative to the initial hardness. For each NBR type, the addition of alcohol (ethanol or isobutanol) further decreased the hardness by 5 to 10 points, and in most cases the aggressive ethanol was a more effective softening agent than aggressive isobutanol.

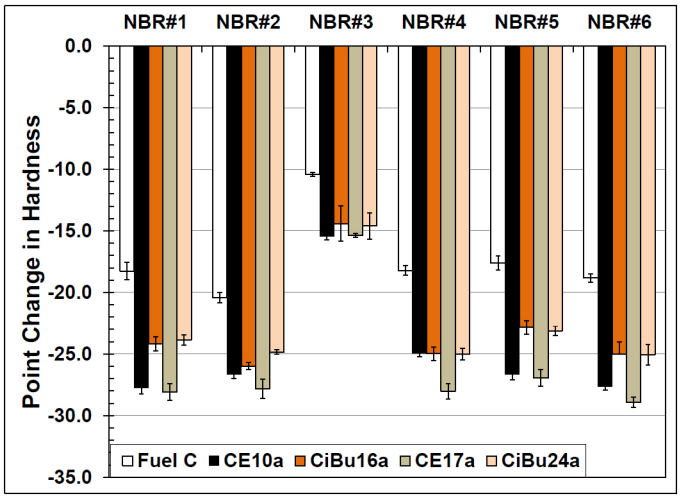

Figure 12. Point change in wet hardness results for the NBR specimens.

All of the NBRs experienced a hardness increase (embrittlement) after drying at 60°C for 20 hours as shown in Figure 13. Interestingly, the marine grade (NBR#3) was much less affected than the other NBR types. The results suggest that Fuel C is the fuel component most responsible for the observed hardness change. In fact, for many of the NBR grades, the addition of ethanol or isobutanol to Fuel C actually reduced (albeit slightly) the extent of hardness change from the original condition. Except for CE10a, which produced a hardness increase matching that of Fuel C for NBR#2, NBR#3, and NBR#6, the remaining test fuels produced similar results to each other.

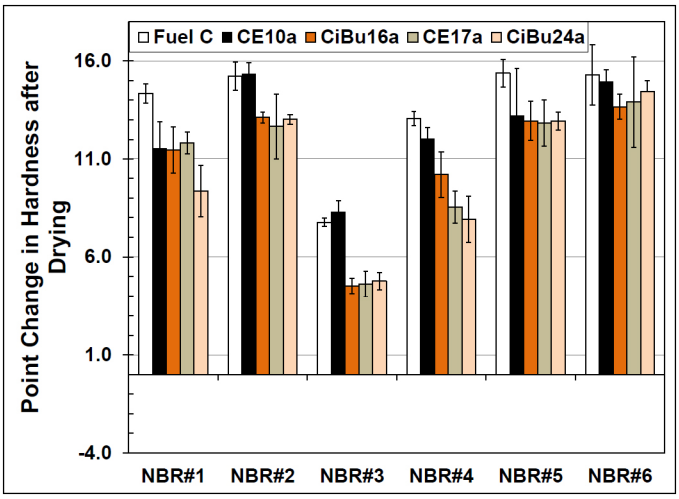

Figure 13. Point change in hardness results for the NBR specimens after drying at 60°C for 20 hours.

Glass Transition Temperature Results

In contrast to the fluorocarbons, the T_g's for the six NBR grades were raised to higher temperatures as shown in Figure 14 following exposure to the test fuels. Each NBR specimen exhibited reduced volume and increased hardness following drying, which is an indication that the plasticizer had been extracted by the test fuels. For the specimens exposed directly to the test fuel liquids, Fuel C raised the glass transition temperature by the highest level.

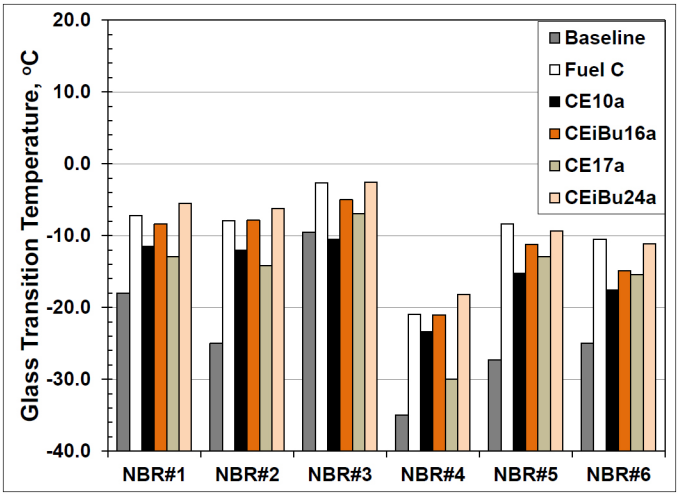

Figure 14. Glass transition temperature results for the NBR specimens after drying at 60°C for 20 hours.

In general the addition of ethanol produced lower T_g values than did equivalent levels of isobutanol. In fact, for several NBRs (NBR#2, NBR#4, NBR#5, and NBR#6), the T_g results were similar for Fuel C and CiBu24a exposures.

Polyurethane, Neoprene, SBR and Silicone

Volume Change

A comparison of the ethanol and isobutanol swelling results for the remaining elastomers (polyurethane, neoprene, SBR, and silicone) is shown in Figure 15. Each of these materials exhibited significantly higher swelling in the test fuels than either the fluoroelastomers or the NBR samples. This result was predicted by the solubility curves for neoprene, SBR, and silicone, but not for polyurethane.

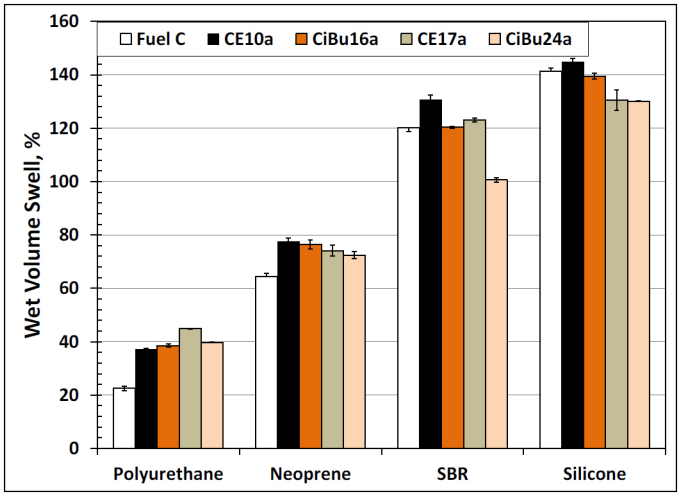

Figure 15. Wet volume swell results for polyurethane, neoprene, SBR, and silicone.

Neoprene swelled approximately 65% with exposure to Fuel C liquid, and adding 10% and 17% aggressive ethanol increased the volume by 79 and 75%, respectively. The level of swell accompanying the isobutanol fuels was slightly lower than the results for equivalent levels of ethanol. These high levels of swelling roughly correspond to the moderate to high solubility numbers predicted in Figure 4.

The volume of the SBR specimen expanded approximately 120% with Fuel C exposure. The addition of 10% aggressive ethanol increased the swelling to 130%, but 17% ethanol lowered the value to around 125%. The test fuels containing isobutanol produced lower swelling than the ethanol blends. In fact, CiBu16a produced the same level of swell as Fuel C, and CiBu24a produced 100% swell, which was 20% lower than the volume obtained with Fuel C. SBR was also observed to be sensitive to the concentration of isobutanol; CiBu24a produced lower swelling than CiBu16a. It is important to note that high swelling was predicted by the solubility curves for SBR.

The dried volume change results for these materials are shown in Figure 16. Polyurethane underwent a 1-2% decrease in volume following exposure to Fuel C, but exposure to CE10a and CE17a resulted in dry-out shrinkages of 12 and 7%, respectively. In contrast, the added isobutanol caused polyurethane to shrink around 5%. The reduced volume is an indication that isobutanol is likely more compatible with polyurethane than ethanol.

Neoprene exhibited the highest level of shrinkage (following dry-out) of the elastomers tested. It was observed to shrink around 18 to 20% following dry-out after being exposed to the test fuel liquids. In this case, Fuel C appears to be the test fuel component most responsible for this effect, with ethanol producing a small additional contribution. The test fuels containing isobutanol produced similar results as Fuel C.

SBR underwent considerable shrinkage (15%) when dried after Fuel C immersion. Aggressive ethanol produced an extra 2% volume contraction, while isobutanol did not provide any added effect. The results suggest that neoprene is slightly more compatible with the test fuels containing isobutanol than with those containing oxygen equivalent levels of ethanol. Silicone rubber (like the fluorosilicone specimen) underwent minimal shrinkage following dry-out.

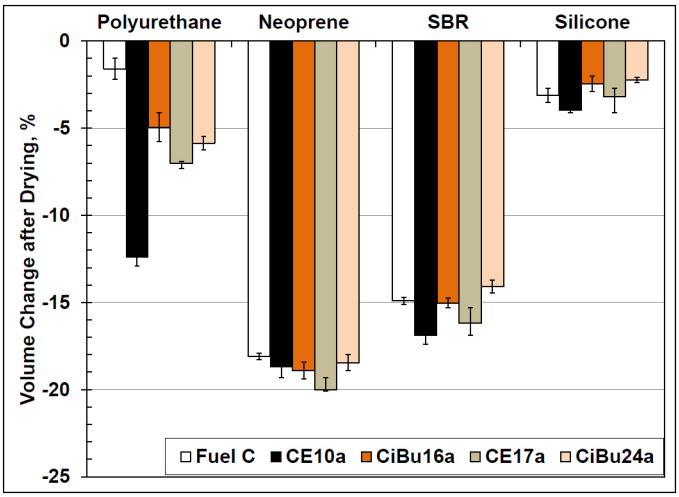

Figure 16. Volume change results for polyurethane, neoprene, SBR, and silicone after drying at 60°C for 20 hours.

Point Change in Hardness

The hardness results for polyurethane, neoprene, SBR, and silicone rubbers (while wet) are shown in Figure 17. The chemical structures for each of these materials are quite different, and this difference is reflected in the extent of softening experienced for each test fuel composition. Exposure to Fuel C produced the least extent of softening in each of the elastomer materials.

Polyurethane was unique among all of the elastomers evaluated in this study in that its hardness was most affected by the alcohols. However, the additions of 10 and 17% aggressive ethanol caused the hardness to drop 40 and 30 points, respectively. Aggressive isobutanol dropped the hardness between 15 and 17 points, which is a significantly

lower decrease than the results for the ethanol blends. The implication is that polyurethane may be more compatible to gasoline containing isobutanol than ethanol.

The hardness values for neoprene dropped around 15 points with exposure to the test fuels. Most of this decrease is attributed to Fuel C as the addition of either alcohol type did not produce any significant additional change. The SBR specimen experienced the highest drop in hardness with exposure to the test fuels. As with the other elastomer types, excluding polyurethane, Fuel C appears to be the component most responsible for the decline in hardness. The two alcohol additives did produce a small additional decrease in hardness, with aggressive ethanol causing slightly more softening than aggressive isobutanol. The original hardness for silicone rubber was reduced 20 points with exposure to Fuel C. The alcohols provided a small (almost insignificant) additional contribution.

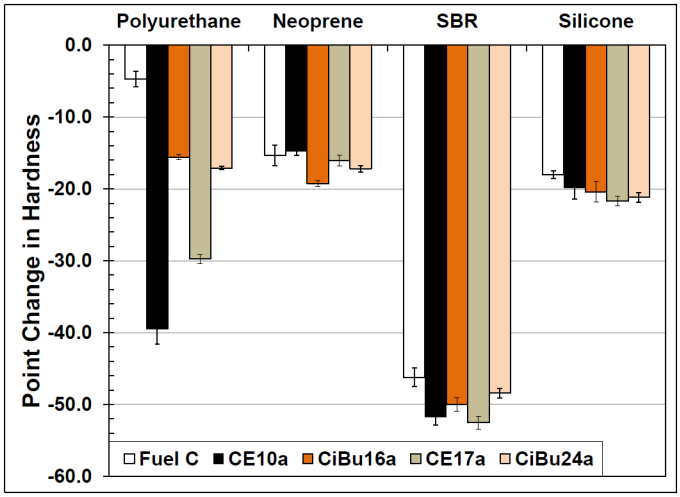

Figure 17. Point change in wet hardness results for polyurethane, neoprene, SBR, and silicone.

The dry-out hardness values for polyurethane, neoprene, SBR, and silicone are shown in Fig. 18. Polyurethane dry-out hardness was unaffected by Fuel C, but this material did post a small drop with exposure with added ethanol and, to a lesser extent isobutanol. Softening in the dried state is an indication of a possible degradation when viewed along with the accompanying shrinkage and wet hardness results.

Figure 18 also shows that neoprene experienced significant embrittlement when exposed to Fuel C. However, the addition of aggressive ethanol or aggressive isobutanol had no observable added effect. SBR did not appear to be affected by Fuel C; however, the addition of ethanol caused a slight increase in hardness, and isobutanol raised the hardness by 5 points (which is still considered low). The dry-out hardness of silicone was essentially unaffected by the test fuels, and it (along with fluorosilicone) were the two elastomers least affected.

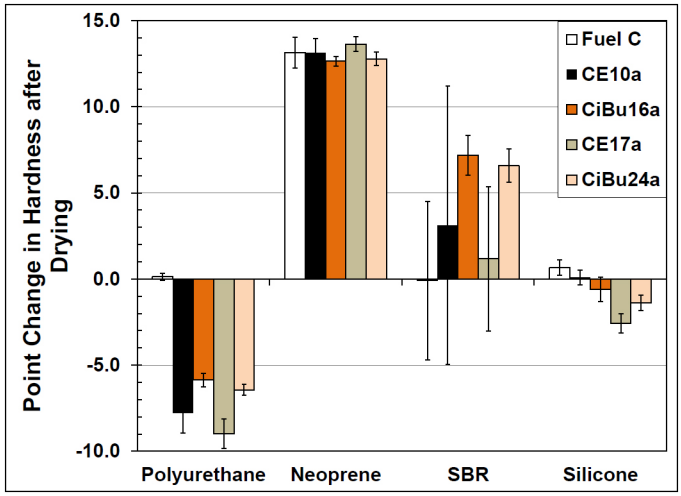

Figure 18. Point change in dry hardness results for polyurethane, neoprene, SBR, and silicone after drying at 60°C for 20 hours.

Transition Temperature

The glass transition temperatures for polyurethane, neoprene, SBR, and silicone rubbers are shown in Figure 19. For these rubber types, the representative specimens showed no significant change to T_g when exposed to the test fuels, either in liquid or vapor form.

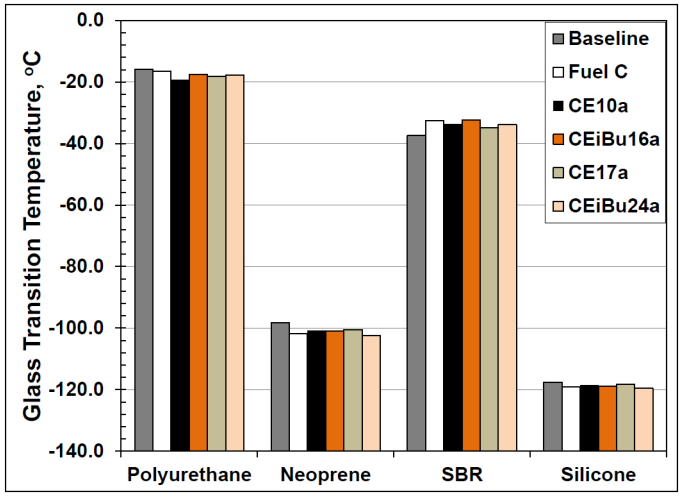

Figure 19. Glass transition temperature results for polyurethane, neoprene, SBR, and silicone after drying at 60°C for 20 hours.

DISCUSSION

Some level of swelling (or volume expansion) upon exposure to gasoline and its blends is expected for elastomeric materials, and this swelling serves to provide a tight seal to prevent leakage. The amount of acceptable volume expansion is highly dependent on the application of the seal, and in fact, volume swelling up to 50% is allowable in many cases. Excessive swelling, however, may cause the seal to extrude beyond the joined interfaces. Protruded seals (or gaskets) are subject to breakage and abrasion. High swelling corresponds

to high fuel permeability, and the potential for polymer component extraction and vapor release (of the fuel through the polymer) exists.

The results for the measured volume swell for each material class are ranked according the measured extent of swell from lowest to highest, along with corresponding ranking of predicted solubility as shown in Table 2. The measured swell corresponds well to the predicted level of solubility, with two notable exceptions; polyurethane and neoprene. The likely reason for this discrepancy is that the parameters for these two materials selected for the solubility analysis were not correctly identified for the particular grades in the evaluation. The Hansen solubility parameters must match the grade of a particular elastomer type. This information was not available and generic parameters were used in most cases.

Table 2. Comparison of the predicted solubility material ranking to the measured swell results.

Ranking	Predicted Solubility	Measured Volume Swell
1	Polyurethane	Fluoroelastomers
2	Fluoroelastomers	NBR
3	Neoprene	Polyurethane
4	NBR	Neoprene
5	SBR	SBR
6	Silicone	Silicone

It is important to note that the results for polyurethane indicate that this material chemically reacted with the alcohol component of the CE10a, CE17a, CiBu16a and CiBu24a test fuels. Chemical reactions are not accounted for in the solubility analysis would negatively affect the accuracy and interpretation of this method.

SUMMARY/CONCLUSIONS

In general, the solubility analysis was good in predicting the extent of swell for the materials exposed to Fuel C and the test fuels containing ethanol and isobutanol. Precise determination of the solubility parameters for each material grade should enable a more accurate estimate of potential swell.

For each elastomer, the gasoline test fuel, Fuel C, was primarily responsible for the observed swelling and softening. The addition of aggressive alcohol to the base fuel, whether as isobutanol or ethanol, produced additional swelling for most materials. The extent of additional swelling produced with the isobutanol test fuels, CiBu16a and CiBu24a, was either similar to, or noticeably less than, that produced with oxygen-equivalent levels of ethanol (i.e., CE10a and CE17a). For SBR and silicone rubbers, 16% aggressive isobutanol showed no change in swell from the Fuel C baseline. However, 24% aggressive isobutanol did produce significantly lower swelling than Fuel C.

The observed swelling was accompanied by a hardness decrease (or softening) from the original condition. For the fluorocarbon and fluorosilicone rubbers, the level of softening corresponded to the increase in volume, and ethanol was found to produce the most softening. The NBR specimens exhibited uniform swelling with all test fuels, but the alcohol additions, especially ethanol, produced significant additional softening. The alcohol additions also produced slight increases in softening for neoprene, SBR, and silicone. Polyurethane was unique in that it was the only elastomer that, when wetted, was not appreciably softened by Fuel C. However, when aggressive ethanol is added, the hardness decreases dramatically. Isobutanol also caused polyurethane to soften, but not nearly as much as was observed with ethanol.

The exposed samples were dried at 60°C for 20 hours to determine if the test fuels were effective at dissolution and extraction of one or more elastomer components, especially plasticizer additions. Plasticizers are typically phthalate chemicals, which are added to certain rubbers to improve pliability. The increased pliability improves the compression properties of the elastomer to provide a better seal. Removal of the plasticizers will cause the rubber to become brittle and potentially crack under compression. This embrittlement is accompanied by an increase in hardness from the baseline value.

After drying, both silicone and fluorosilicone returned to their original volume and hardness levels, indicating that neither of these elastomer types was structurally affected by the test fuels. The fluorocarbons showed a small volume increase and drop in hardness after drying that was attributed to the retention of the test fuel in their microstructure. The NBR samples all exhibited a high level of shrinkage (10-18%) and embrittlement. In all cases Fuel C was the fuel component primarily responsible for shrinkage, although ethanol did produce a small additional contribution. Isobutanol, on the other hand, was observed to have no added effect on NBR shrinkage. Interestingly, embrittlement was actually slightly reduced for those test fuels containing ethanol and isobutanol, with isobutanol producing the lowest levels of embrittlement for the NBRs. Neoprene and SBR exhibited shrinkage with exposure, but virtually all of this effect was caused by Fuel C. Fuel C also appears to be the primary factor causing neoprene embrittlement, whereas SBR was unaffected, except for a slight embrittlement when exposed to the test fuels containing isobutanol. The addition of aggressive ethanol to the base fuel did not produce any additional shrinkage or embrittlement in either neoprene or SBR.

Analysis of the DMA test results showed that glass transition temperature was unaffected by the test fuels for fluorosilicone, polyurethane, neoprene, SBR, and silicone. The fluorocarbons showed a slight drop (10°C) in the transition temperature following exposure to the test fuels, whereas the NBRs exhibited around a 20°C increase in transition temperature. In these cases, Fuel C was the component primarily responsible for the shift in the transition temperature from baseline.

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DEFINITIONS/ABBREVIATIONS

ASTM - American Society for Testing and Materials

CE10a - test fuel composed of 10 vol.% aggressive ethanol and 90 vol.% Fuel C

CE17a - test fuel composed of 17 vol.% aggressive ethanol and 83 vol.% Fuel C

CiBu16a - test fuel composed of 16 vol.% aggressive ethanol and 84 vol.% Fuel C

CiBu24a - test fuel composed of 24 vol.% aggressive ethanol and 76 vol.% Fuel C

d_S - solubility distance

DMA - dynamic mechanical analysis

DOE - US Department of Energy

E0 - neat gasoline

E10 - gasoline containing 10 vol.% ethanol

E15 - gasoline containing 15% vol.% ethanol

EPA - US Environmental Protection Agency

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

HSP - Hansen solubility parameter

IR - interaction radius

LMW - low molecular weight

NBR - acrylonitrile butadiene rubber

ORNL - Oak Ridge National Laboratory

SAE - Society of Automotive Engineers

SBR - styrene butadiene rubber

T_g - glass transition temperature