

Compatibility of elastomers with test fuels of gasoline blended with ethanol

Michael Kass, Timothy Theiss, Chris Janke and Steve Pawel, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA; and J. Thomas Chapin, Edwin Yang and Ken Boyce, Underwriters Laboratories, Northbrook, Illinois, USA

This article summarises the compatibility of six elastomers – used in fuel storage and delivery systems – with test fuels representing gasoline blended with up to 85% ethanol. Individual coupons were exposed to test fuels for four weeks to achieve saturation. The change in volume and hardness, when wetted and after drying, were measured and compared with the original condition.

Ethanol is becoming more widely used as a renewable transportation fuel or fuel additive in the USA and Brazil. The use of ethanol to displace gasoline consumption is expected to grow and many other countries are examining its potential as part of their overall energy strategies for transportation fuels.

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 (USEPA). However, in 2009, the USEPA approved a waiver to allow the use of 15% ethanol in gasoline (E15).^[1]

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 E0 use. In 2008, the US Department of Energy (DOE) initiated a series of studies to investigate the impact of fuel ethanol on materials commonly used for fuel storage and dispensing. The results of these studies have been published in two reports that cover selected mechanical properties of sealants, metals, plastics and elastomers with exposure to fuel ethanol.^[2,3]

Elastomeric materials are used in hoses and in non-structural sealing applications throughout the fuelling infrastructure. 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 gasoline fuels mixed

with ethanol, in order to provide guidance on proper seal material selection, and identify potential leak sites in fuelling hardware.

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 by calculating the difference in the solubility parameters between the two components using the Flory–Huggins solution theory.^[4]

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 and ethanol are shown in **Figure 1** as a simplified means of displaying this effect.

As shown, the total solubility of gasoline–ethanol blends increases linearly with ethanol content. Also depicted in the figure is the typical range of solubility parameters for many elastomers. As the

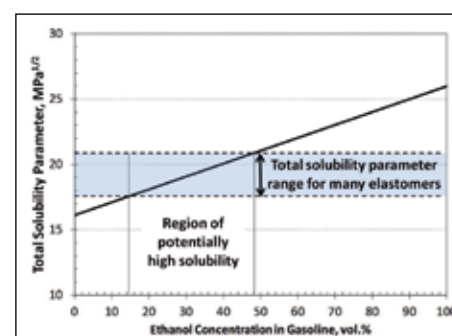


Figure 1. Total solubility parameter for gasoline–ethanol fuel mixtures. The blue horizontal band represents the solubility range of many dispenser elastomers.

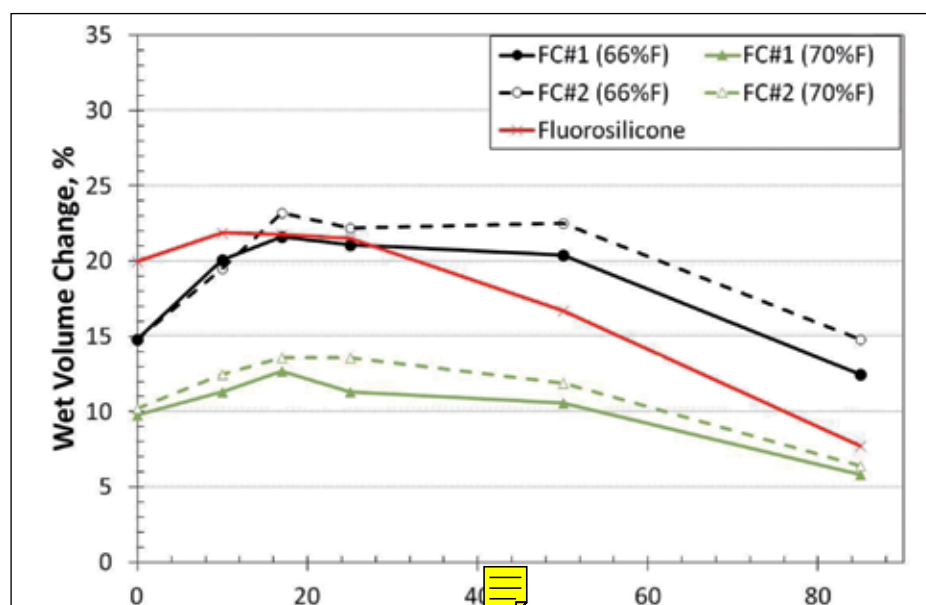


Figure 2. Wet volume change results for four fluorocarbons and one fluorosilicone sample in gasoline–ethanol fuel mixtures.

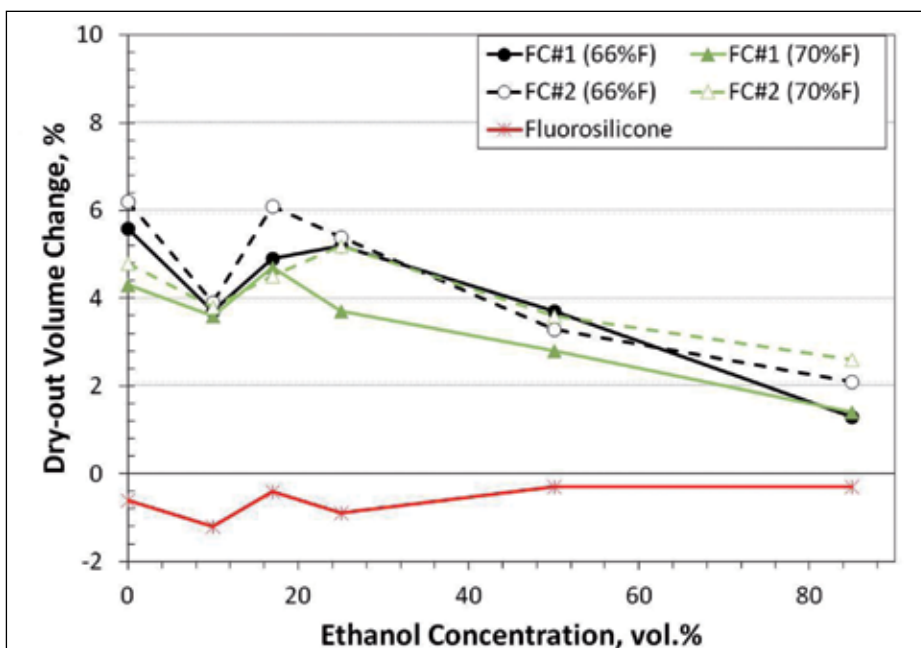


Figure 3. Point change in hardness (wetted) for four fluorocarbons and one fluorosilicone sample in gasoline-ethanol fuel mixtures.

ethanol concentration increases from 0% to 15%, the solubility parameter of the fuel approaches the values of many elastomers and, therefore, the potential for higher solubility, and hence polymer swelling and fuel permeation, is also enhanced. 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, plasticisers, stabilisers, 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.

Materials and test methodology

This study consisted of a side-by-side analysis of different elastomer materials under controlled conditions.

The elastomers included four types of fluorocarbon rubbers, one fluorosilicone rubber, one silicone rubber, six nitrile rubbers (NBRs), one styrene butadiene rubber (SBR), one neoprene and one polyurethane. These elastomers con-

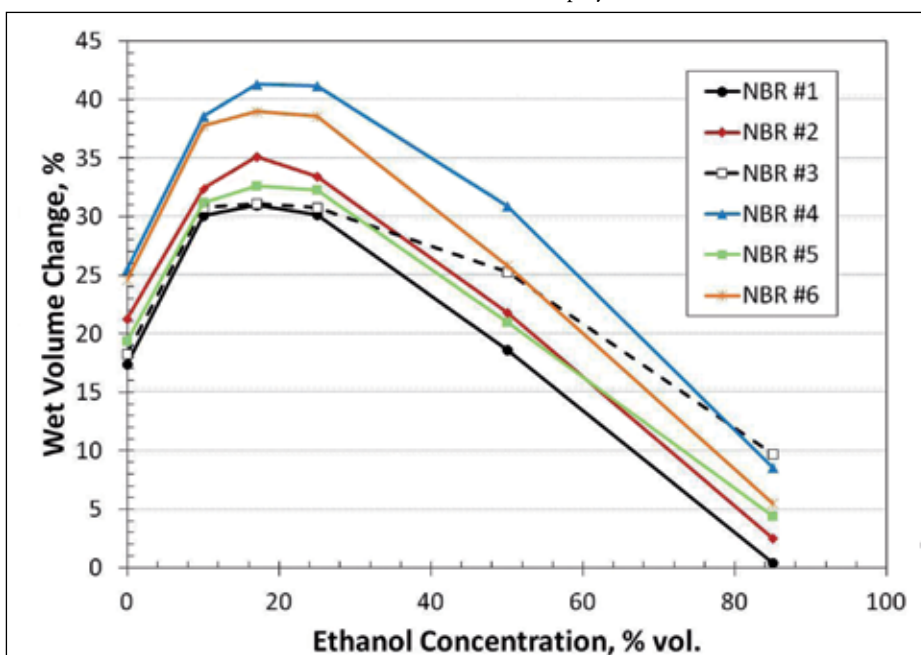


Figure 4. Wet volume change results for six nitrile rubber materials in gasoline-ethanol fuel mixtures.

tained different types and levels of LMW additives which may be affected from fuel exposure.

The four fluorocarbon samples were supplied by two manufacturers, who provided two samples each. These samples are labelled as FC #1 or FC #2 to denote the supplier. In addition to supplier designation, the sample labels also include fluorine concentration, and both suppliers provided samples that contained 66% and 70% fluorine.

Each elastomer sample was cut into rectangular specimens and evaluated using Fuel C, CE10a, CE17a, CE25a, CE50a and CE85a. These test fuels are based on the Fuel C composition and aggressive ethanol formulations described in Society of Automotive Engineers' (SAE) standard 'J1681 – Gasoline, Alcohol, and Diesel Fuel Surrogates for Materials Testing'.^[5]

Fuel C is a 50–50 mixture of toluene and isooctane and is representative of highly aromatic gasoline (greater than 40% aromatics by volume). The other test fuels contain an aggressive ethanol solution added to Fuel C. The numbers that follow CE refer to the volume fraction of ethanol added to Fuel C, and the use of aggressive ethanol (containing water and trace levels of sodium chloride, acetic and sulfuric acids specified in SAE J1681) is represented by the "a". These contaminants are found in ethanol-gasoline fuels and represent potential high contamination conditions for fuel-grade ethanol. CE17a was selected as a worst-case representative of E15, since surveys have shown that the actual ethanol content in E10 can vary by up to 2%.

Three specimens (measuring 1.3 cm wide by 3.8 cm long by 0.25 cm thick) were prepared from each elastomer type and the mass, volume and hardness of each pre-exposed specimen was measured. The specimens were then mounted on a cylindrical liner which was placed inside a 170-litre sealed stainless steel chamber. All specimens were completely submerged in the test fuels, and the sealed tanks were heated to 60°C for four weeks. During this period the fuel was stirred continuously to maintain a flow rate of 0.8 m/s past the specimens.

Following each run, the specimens' mass, volume and hardness were remeasured to determine the influence of wet conditions. The samples were then dried at 60°C for 20 hours. The wetted and dried property changes were compared with the original untreated specimens to assess property degradation.

Significance of volume and hardness

The two primary means of assessing compatibility between polymers and solvents involve measuring the change in hardness and volume

of the solid material when it is fully saturated (wet) and after drying.

Volume change is essentially interchangeable with mass change, and the studies on which this article is based showed a linear correlation of volume and mass – when wetted and after drying.

Volume expansion indicates fuel permeation of the solvent into the solid material and potential dissolution of one or more components. Some volume expansion is expected and beneficial by maintaining a tight seal, however, excessive swelling may cause elastomer extrusion past the joined interface, where it may become susceptible to damage.

When swelling is accompanied by a significant loss of hardness (or softening) in the elastomer, then the sealing forces are weakened and leakage may occur between the seal and the joined interface. For hose-type applications, excessive swell may cause buckling or high stresses leading to a compromise in durability.

The other concern that arises occurs when the elastomer is allowed to dry. If a solvent successfully dissolves one or more components of the elastomer, then the seal will lose mass and undergo shrinkage. A seal experiencing a high degree of shrinkage will have less material available to afford a proper fit and the sealing forces will be reduced. Excessive shrinkage may create a gap between the joined interfaces or cause cracking in hoses. In either case a leak may result.

Another concern associated with shrinkage is the extraction of a key component – such as a plasticiser or stabiliser – which will increase the hardness of the seal (making it brittle), thereby reducing durability and further increasing the risk of cracking.

Results

The elastomers exhibited various degrees of swelling, depending on type and fuel ethanol concentration. In most cases, the actual physical measurement of the volume swell corresponded to the predicted location of maximum swell, as predicted in Figure 1.

Because of the wide compositional ranges of the fluorocarbons and NBRs, a wide variety of property responses would not be unexpected, however, the results tended to group strongly for elastomer type.

Fluoroelastomers

The extent of volume swell for four fluorocarbons and one fluorosilicone sample varied according to ethanol concentration, as shown in Figure 2 (on page 8). Those samples having identical fluorine concentrations exhibited similar behaviour (independent of the sup-

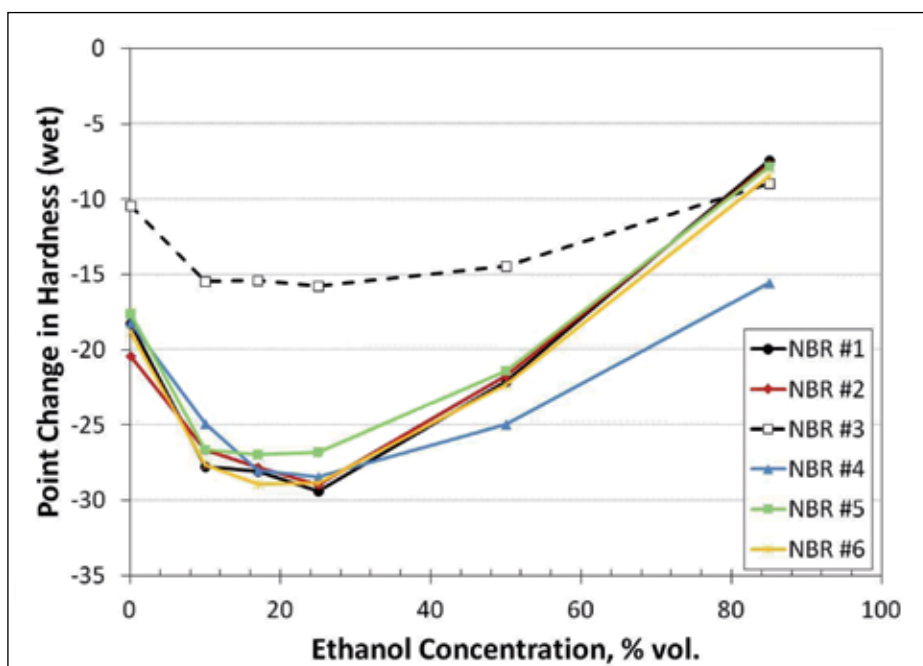


Figure 5. Point change in hardness (wetted) for six nitrile rubber materials in gasoline–ethanol fuel mixtures.

plier), and the degree of swelling was found to increase with decreasing fluorine concentration.

In general, maximum swell occurred at 17–25% ethanol for the fluorocarbon specimens – in agreement with the predicted location of peak swell shown in Figure 1. Fluorosilicone achieved maximum swell at 10% ethanol. Silicone rubber has a lower solubility parameter value than fluorocarbon, therefore, as expected, the ethanol concentration corresponding to peak swell is correspondingly lower. In each case the volume swell declined dramatically with exposure to higher ethanol concentrations, such

that for 85% ethanol the volume swell either matched the value for Fuel C or was lower.

In general, the fluoroelastomers exhibited a small reduction in hardness in the wetted state, which corresponded with fluid adsorption. For most, there was a loose correlation between the change in hardness and the volume swell for the wetted specimens.

The change in both volume and hardness for each specimen was measured after drying at 60°C for 20 hours. The volume change is shown in Figure 3 (on page 8). In contrast to fluorosilicone, all of the fluorocarbon speci-

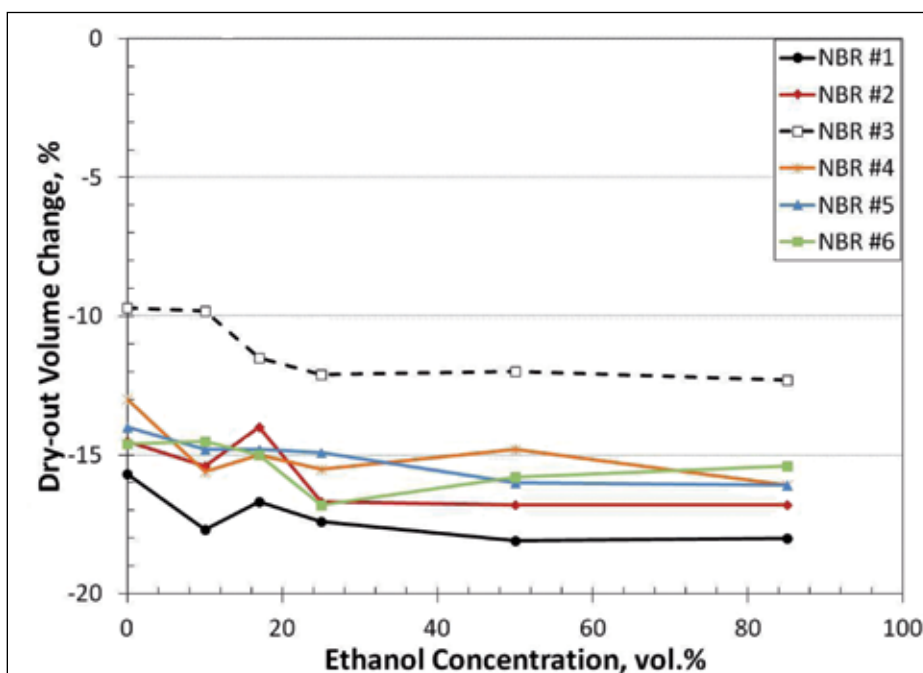


Figure 6. Dried volume change results for six nitrile rubber materials in gasoline–ethanol fuel mixtures.

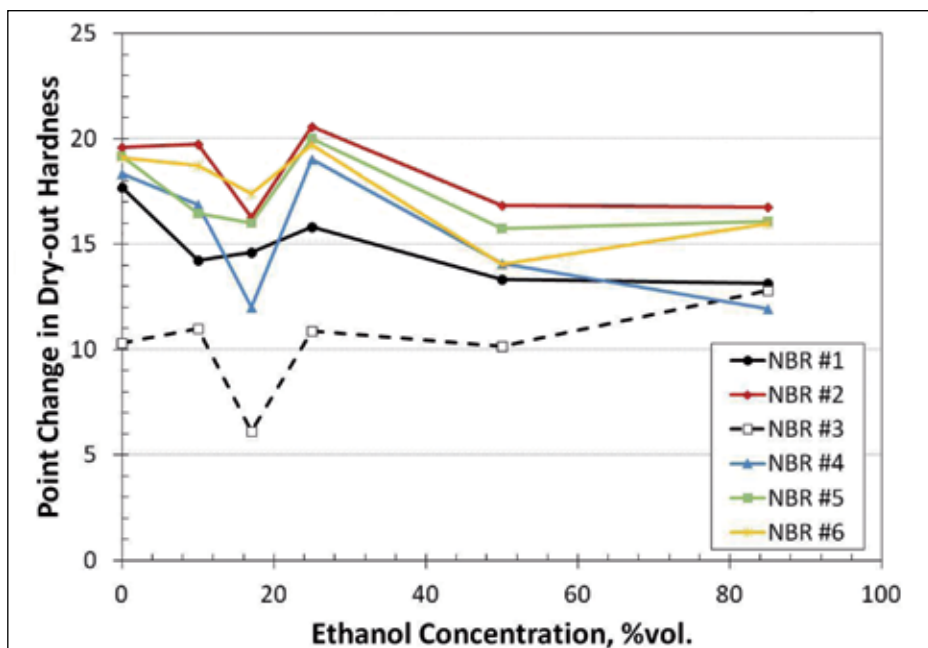


Figure 7. Dried hardness results for six nitrile rubber materials in gasoline-ethanol fuel mixtures.

mens exhibited volume expansion following dry-out. As expected, this increase corresponded with total mass, which indicates that fuel was retained within the elastomer structure. For these materials, this fuel retention was also responsible for the slight drop in hardness following dry-out. Fuel retention in fluoropolymers has been observed by other investigations¹⁶ and has also been noted for some plastic materials.

The relationship between dry-out volume (and hardness) roughly corresponds to the wetted results, with one major exception. There is a significant drop in both volume and hardness associated with exposure to the CE10a test fuel, but the reason for this dip is unclear. It is possi-

ble that a minor fluorocarbon LMW component was highly soluble at this concentration, and was subsequently extracted during the drying process. Loss of a minor component would not necessarily be noticed from the wetted results since the absorbed fuel mass (and accompanying volume increase) may be large relative to the mass of the extracted component.

NBRs

The volume swelling results for the six NBRs are shown in Figure 4 on page 8).

It should be mentioned that NBR compounds tend to be modified with LMW plasticisers and

other additives. The degree of hardness of these materials is directly related to the amount of nitrile present in the copolymer (that is, a higher hardness is achieved by increasing the nitrile content in the copolymer). The resulting profiles are similar, despite the differences in levels of swell between the samples. NBR #3 was different from the other NBRs in that it was a marine grade rubber and, therefore, it tended to not group as closely with the other NBR types.

For each NBR, volume swell increased to a maximum at around 17–25% ethanol, and then declined sharply with increased ethanol content. Interestingly, the level of swell at 85% ethanol is markedly lower than the Fuel C values, and for NBR #1 the difference between the original and exposed volumes was negligible. This result shows that NBRs are less soluble in gasoline blends containing high levels of ethanol and corresponds to the relative solubility distances in Figure 1, which predicts lowered solubility for fuel containing high ethanol concentrations.

The accompanying wet hardness results (Figure 5, on page 9) show a strong correlation with the volume change. Not surprisingly, the highest drop in hardness coincides with the location of maximum swell. However, it is interesting to note that although the volume of NBR #1 was unchanged by exposure to CE85a, the hardness declined by seven points, indicating that some level of permeation of the rubber, by the test fuel, had occurred.

Following dry-out, each NBR material exhibited significant shrinkage and embrittlement because of LMW extraction, as depicted in Figure 6 (on page 9) and Figure 7, respectively. Most of the volume contraction occurred with exposure to Fuel C. The added ethanol did contribute to the overall shrinkage, but only to a small extent. For each case, except NBR #3, volume contraction was approximately 15–17%. On the other hand, NBR #3 contracted by around 10%.

The dry-out hardness (Figure 7) increased significantly, but, as in the case of the volume, the hardness did not appear to be significantly affected by ethanol (although a small decline in hardness was noted for several NBR types exposed to CE17a). This increase in hardness, when combined with the loss of volume and mass, is a strong indication that plasticisers had been extracted by the test fuels – the fuel component most responsible was Fuel C.

Polyurethane, neoprene, SBR and silicone rubbers

The wet volume and hardness results for the remaining elastomers are shown together in Figure 8 and Figure 9 (on page 11), respectively.

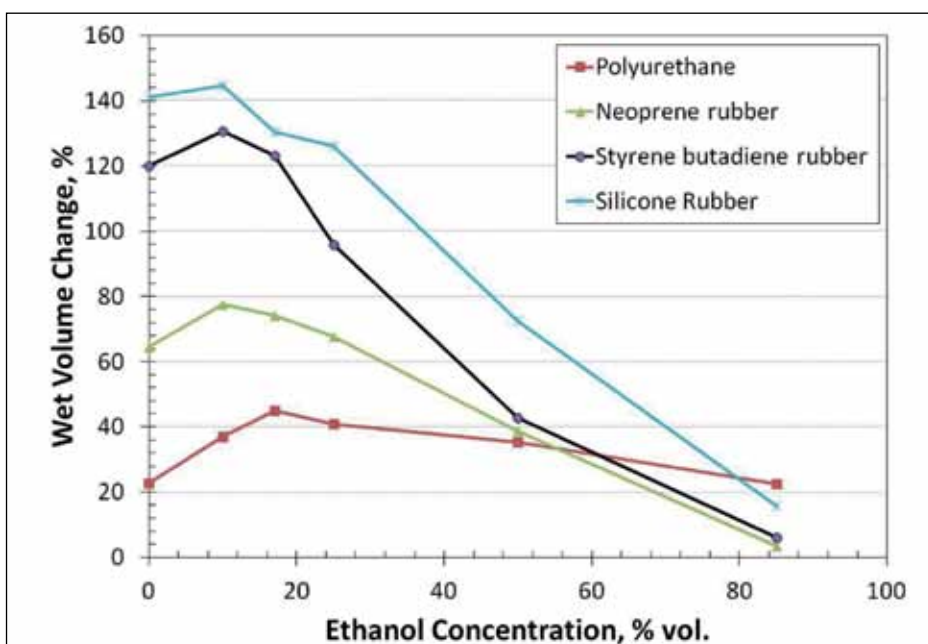


Figure 8. Wet volume change results for polyurethane, neoprene, styrene butadiene rubber and silicone rubber in gasoline-ethanol fuel mixtures.

Each of these elastomer types swelled considerably with exposure to Fuel C. Neoprene, SBR and silicone all exhibited maximum swelling at 10% ethanol, while polyurethane peaked at 17% ethanol. The swelling behaviour of neoprene, SBR and silicone follows the trend exhibited by the NBR. That is, following peak swell the volume declined with higher ethanol concentrations, such that the values for 85% ethanol were lower than those for Fuel C. Polyurethane showed similar behaviour, except that the volume at 85% ethanol matched the value for Fuel C.

Consistent with the NBRs, the wet hardness declined with volume swell. Interestingly, although silicone experienced the highest extent of swelling, it did not soften as dramatically as SBR and polyurethane.

The corresponding dry-out volume and hardness changes are shown, respectively, in **Figure 10** and **Figure 11** on page 12. Neoprene and SBR lost significant volume (18% and 15%, respectively) with exposure to each test fuel composition. For these two elastomers, the extent of shrinkage was unaffected by ethanol, indicating the Fuel C was predominantly responsible for this effect.

Comparison of the dry-out hardness change shows that neoprene became embrittled after drying, while silicone and SBR were only slightly affected (if at all). For neoprene, the volume reduction and hardness increase are highly indicative of plasticiser extraction. In contrast to the other materials, polyurethane exhibited very low swell and change in hardness with exposure to Fuel C, but did shrink by about 10% (after drying), with exposure to ethanol.

Likewise, the dry-out hardness for polyurethane was also unaffected by Fuel C, but dropped noticeably when ethanol was present. This softening, combined with volume loss, is a strong indication that the polyurethane experienced permanent chemical degradation when exposed to fuel-borne ethanol.

Although the silicone rubber specimen exhibited the highest degree of peak swelling, it was least affected by drying. There was a small level of shrinkage (3%) that occurred following dry-out, but the hardness returned to the baseline value.

Summary

- In general, there was good to excellent agreement between the predicted solubility behaviour and the actual volume swell measurements. All of the elastomers exhibited peak swell for intermediate (10–17%) levels of ethanol. In most cases the wet volume swell results obtained

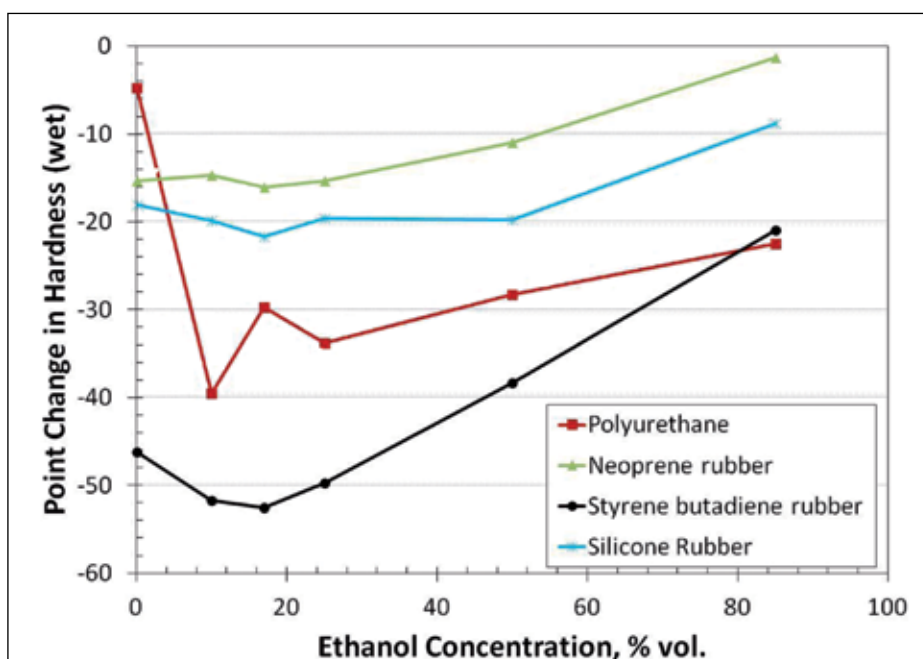


Figure 9. Point change in hardness (wetted) for polyurethane, neoprene, styrene butadiene rubber and silicone rubber in gasoline–ethanol fuel mixtures.

at 85% ethanol were lower than the observed swell at E0 (or Fuel C). This was especially true for several NBRs, SBR, neoprene and silicone.

- In general, fluoroelastomers swelled the least when exposed to gasoline containing ethanol. Following dry-out some fluid is retained in the structure, which results in a slight increase in dry-out hardness from the original condition. For the fluorocarbons, a higher volume swell was observed for those samples that have a higher fluorine content. NBR, SBR, silicone, neoprene and polyure-

thane exhibited relatively high swell, which peaked in test fuels containing 10–17% ethanol.

- The NBR samples and neoprene showed significant volume loss and hardening following dry-out, indicating plasticiser extraction. SBR also lost significant volume after drying, however, the hardness was unaffected and, therefore, plasticiser dissolution had not occurred for this material.
- NBR, SBR, neoprene and polyurethane exhibited relatively high swell, which

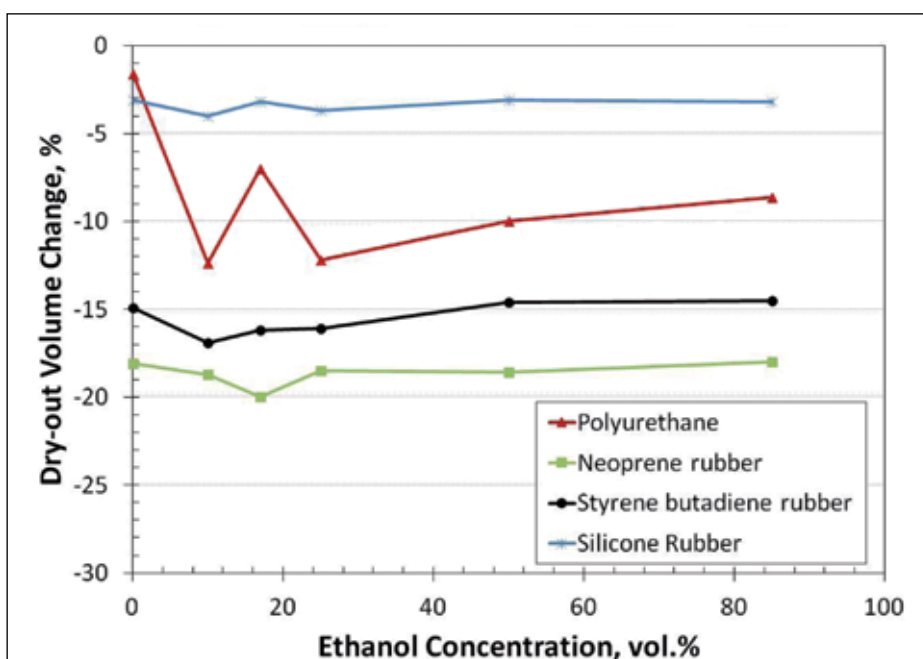


Figure 10. Dried volume change results for polyurethane, neoprene, styrene butadiene rubber and silicone rubber in gasoline–ethanol fuel mixtures.

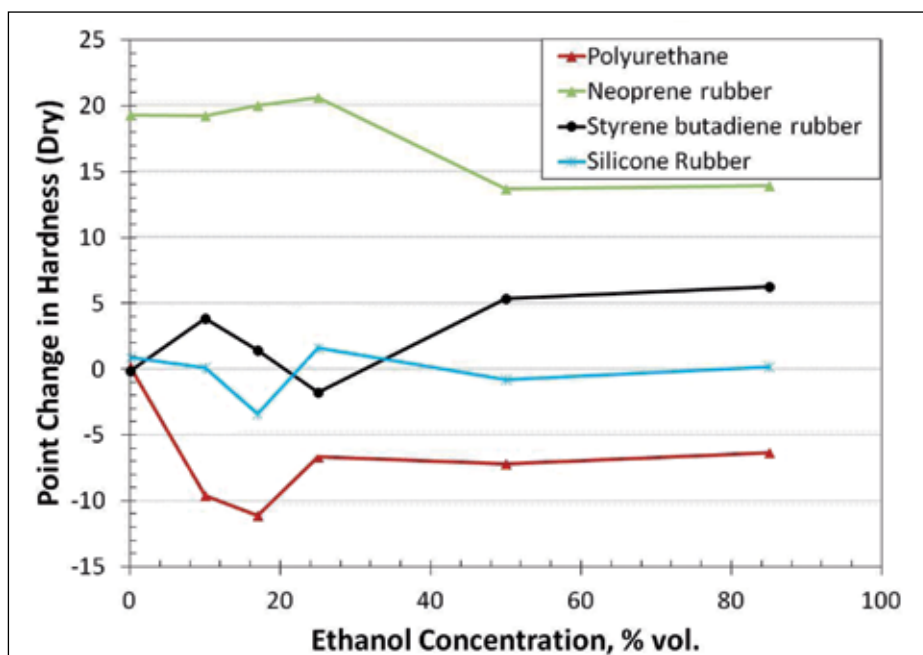


Figure 11. Dried hardness results for polyurethane, neoprene, styrene butadiene rubber and silicone rubber in gasoline-ethanol fuel mixtures.

peaked in test fuels containing 10–17% ethanol. At 85% ethanol, negligible volume swell occurred for several NBR types and SBR, however, the dry-out properties indicated that plasticiser extraction had, in fact, occurred in spite of the lack of swell.

- Silicone rubber swelled to the highest extent when wetted by Fuel C and small additional amounts of ethanol. After drying, it exhibited a small reduction in volume compared with the pre-tested condition and the hardness was unaffected.
- Polyurethane appears to be unaffected by Fuel C, however, the presence of ethanol has a negative effect on the sealing properties and indications are that structural degradation had occurred.

Acknowledgements

This effort was part of a larger material compatibility study sponsored by the Biomass, Clean Cities and Vehicle Technology Programs within the US DOE's Office of Energy Efficiency and Renewable Energy. The authors gratefully acknowledge the support and guidance of Steve Przesmitzki, Dennis Smith, Kevin Stork, Joan Glickman, Alicia Lindauer, Shab Fardanesh and Brian Duff.

References

1. USEPA Web-site: www.epa.gov/otaq/regs/fuel/additive/e15#wn
2. Kass, M.D., Theiss, T.J., Janke, C.J.

Pawel, S.J. and Lewis, S.A., 'Intermediate Ethanol Blends Infrastructure Materials Compatibility Study: Elastomers, Metals, and Sealants', Oak Ridge National Laboratory Technical Memorandum ORNL/TM-2010-326, March 2011.

3. Kass, M.D., Theiss, T.J., Janke, C.J. and Pawel, S.J., 'Compatibility Study for Plastic, Elastomeric, and Metallic Materials Exposed to Aggressive Formulations of Ethanol-blended Gasoline', Oak Ridge National Laboratory Technical Memorandum ORNL/TM-2012-88, May 2012.
4. 'Hansen Solubility Parameters: A User's Handbook' (second edition), C.M. Hansen. CRC Press, New York, USA (2007).
5. Society of Automotive Engineers, 'Gasoline, Alcohol, and Diesel Fuel Surrogates for Materials Testing', SAE J1681 (issued September 1993 and revised 1 January 2000).
6. Jones, B., Mead, G., Steevens, P. and Connors, C., 'The Effects of E20 on Elastomers used in Automotive Fuel System Components', Minnesota Center for Automotive Research, Minnesota State University, Mankato, USA, 22 February 2008.

Contact:

Michael Kass, Oak Ridge National Laboratory, NTRC Bldg, 2360 Cherahala Blvd, Knoxville, TN 37932, USA. Tel: +1 865 946 1241, Email: kassmd@ornl.gov, Web: <http://feerc.ornl.gov>

(This feature is based on an article, submitted by the authors, entitled 'Compatibility of fueling infrastructure elastomers to test fuel formulations representing blends of ethanol and gasoline'.)