

Compatibility of Fuel System Elastomers with Bio-Blendstock Fuel Candidates Using Hansen Solubility Analysis

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ABSTRACT

The compatibility of key fuel system infrastructure elastomers with promising bio-blendstock fuel candidates was examined using Hansen solubility analysis. Thirty-four candidate fuels were evaluated in this study including multiple alcohols, esters, ethers, ketones, alkenes and one alkane. These compounds were evaluated as neat molecules and as blends with the gasoline surrogate, dodecane and a mix of dodecane and 10% ethanol (E10D). The elastomer materials were fluorocarbon, acrylonitrile butadiene rubber (NBR), styrene butadiene (SBR), neoprene, polyurethane and silicone. These materials have been rigorously studied with other fuel types, and their measured volume change results were found to correspond well with their predicted solubility levels. The alcohols showed probable compatibility with fluorocarbon and polyurethane, but are not likely to be compatible at low blend levels with NBR and SBR. Low and mid-range blends are also considered incompatible with silicone, as are mid-range blends with neoprene. The alkane fuel candidate is likely compatible with fluorocarbon, polyurethane, NBR and SBR at most blend levels, but low to mid-range blends are not likely compatible with silicone. Neoprene showed compatibility only with mid-range blends of the alkane. The alkene and aromatics exhibited similar compatibility. They showed good compatibility with fluorocarbon, neoprene and polyurethane, but not with silicone, NBR, and SBR. For the esters, compatibility varied depending on the ester type. Generally, these fuels were compatible with fluorocarbon and polyurethane, but not with silicone. Low blend levels are likely to be compatible with neoprene, but considerable uncertainty is noted for NBR and SBR. Ethers were generally compatible with fluorocarbon and at low blend levels with neoprene and polyurethane. They were most incompatible with silicone, NBR, and SBR. The ketones were the one fuel type that showed some incompatibility with fluorocarbon, especially at high blend levels. Incompatibilities were also noted for silicone, neoprene and polyurethane. However, ketones are likely compatible with NBR and SBR at high blend levels.

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INTRODUCTION

Background

The chemistry of transportation fuels has undergone changes over time. Some of these changes are dramatic; such as the removal of tetraethyl lead and methyl tert-butyl ether (MTBE) from gasoline, but most are more subtle and gradual in nature. With each new change or additive, a change in properties is also observed. Currently the desire to utilize renewable resources and reduce dependency on petroleum derived fuels is a primary motivator for developing new fuels as demonstrated by the addition of ethanol to gasoline. New fuel chemistries are now being developed to optimize combustion for improved engine performance (efficiency and power) and for reduction of greenhouse gas emissions. As these fuels are being developed and considered, it is critical that their compatibility with materials commonly used in fuel storage and delivery systems are assessed. Failure to properly assess potential incompatibilities (with new fuel chemistries) prior to new fuel introduction may result in seal failures and subsequent fuel leakages [1]. For metallic materials incompatibility is fairly well understood and is almost always related to one or more of the following:

- the presence a separate aqueous phase allowing acid formation,
- chemical degradation (or oxidation) of methyl esters to form acids,
- the presence of acids either as a fuel component,
- a secondary reaction with container polymers (such as with an acetate resin), or
- via microbial action (which requires an aqueous phase).

For many polymers, fuel compatibility is primarily determined by the mutual solubility existing between the polymer and the fuel (also known as the solute and solvent, respectively). Solubility can also exacerbate susceptibility to chemical attack, although most of the elastomers evaluated in this study are not considered to be chemically reactive to many fuel types. One exception is polyurethane, which has been shown to be reactive to ethanol [2].

Solubility generally leads to swelling or volume expansion, though other important physical properties (especially those related to sealing) are also affected. These properties, which include hardness, elastic modulus, compression set, etc., impact the ability of an elastomer to provide a durable and effective seal. Because of the expense and complexity associated with measuring these additional

properties, the majority of elastomer seal manufacturers use only the volume expansion to rate compatibility [3, 4, 5, 6, 7]. However, high volume expansion, even at levels exceeding 50%, does not necessarily mean that a fuel is incompatible with a given polymer. The application also needs to be considered. Some level of swelling is desirable and helps to provide a tight seal at the interface. However, excessive swelling may cause extrusion and the potential for structural damage. For static applications, moderate to high swelling (25-50%) may be acceptable. However, dynamic applications typically require swelling levels below 25% to prevent seal damage and maintain design durability.

In 2015, the United States Department of Energy initiated a multi-laboratory and multi-year effort to co-optimize fuels and engines known as the co-optima project [8]. Early activities included identifying potential fuel candidate molecules to be evaluated for their combustion, chemistry, and compatibility properties with current and advanced engine concepts. One of those early studies identified over 35 bio-blendstock single compounds and blend formulations to be considered as potential fuel candidates [9]. None of these fuel candidates contain acids or olefin branches susceptible to acid formation (in the case of esters). As such, they are not considered corrosive to infrastructure metals. Polymer compatibility, on the other hand, is governed by the level of mutual solubility existing between the polymer and the fuel. Several studies have shown that many polymers, especially elastomers, exhibit pronounced solubility (or swell) when exposed to oxygenates such as ethanol-blended gasoline [2,10–11].

Elastomers, and their potential compatibility with identified co-optima high-octane fuel candidates, are the subject of this report. These materials are widely used as seals and flexible hoses. As seals, their purpose is to provide a leak-tight connection between two or more components or systems. Therefore, they are a critical component of most mechanical seals and are usually the limiting component in fluid resistance (compatibility) and range of temperature operation [12]. The properties and capabilities vary considerably among elastomer type and grade. Unfortunately, there is often a lack of understanding of these limitations and the differences associated with the elastomer type. Because of the critical role these materials play in fueling systems, it is of paramount importance to know their compatibility to fuel chemistries before they are introduced in fueling applications.

Compatibility of polymers can be assessed empirically or by analyzing the solubility parameters assigned to a given fuel and polymer. Empirical methods involve measurement of the change in physical properties following exposure to the test fluid for a period of time. Solubility analyses are based on the Flory-Huggins Theory of Solutions and involve comparison of predetermined parameters associated with intermolecular cohesion for both the polymer and test fuel.

Solubility Theory

For polymer materials (such as elastomers) solubility is the ability of the fluid (solvent) to adsorb and dissolve into the polymer itself. The factors governing solubility are best described by the Flory-Huggins Theory of Solutions, and are related to the forces governing intermolecular attraction [13]. Materials having similar

intermolecular forces (such as London dispersion forces, polarity, and hydrogen bonding) will have high solubility. Solubility theory assigns parameters to substances (based on their intermolecular forces). The closer the parameter (or parameters) of one substance is to another, the higher the solubility.

In practice, solubility is empirically assessed by measuring the volume increase of the polymer after it has been exposed to the fuel or fluid of interest. However, in lieu of volume measurement, the solubility potential between a polymer and a fuel can be assessed by calculating the difference in the solubility parameters that are characteristic for the polymer and fuel.

There are several approaches used to assess solubility that are based on Flory-Huggins solution theory, but the two most common are the Hildebrand and Hansen methods. The Hildebrand method is one dimensional and uses a single parameter to represent the total attractive force (van der Waals forces). In contrast, the Hansen method employs three separate parameters representing forces not only associated with dispersion cohesive energy, but also polarity (or dipole moment) and hydrogen bonding. Even though the Hansen method has better applicability than single parameter methods, the results from this approach are still approximations. The Hansen approach is the most widely used and parameters have been determined for a large number of organic materials and solvents. Many of these parameters can be located readily from the literature and a good starting point is the Hansen Solubility Parameters Handbook [13]. Solubility-based analysis studies are important because they can be used to quickly identify fuel blend chemistries and concentrations which are potentially damaging to certain polymer materials. In this study, a Hansen solubility analysis was performed for common fuel systems elastomers and for a number of co-optima high-octane candidate fuel chemistries.

HANSEN SOLUBILITY ANALYSIS

For each material and fluid, the Hansen method assigns a parameter to each of the three cohesive forces (atomic dispersion, polarity, and hydrogen bonding). For the elastomer (or solute), the three parameters define the center of a sphere (labeled A) as shown in [Figure 1](#). The sphere represents a boundary separating highly soluble components from insoluble ones. The radius of the sphere is called the interaction radius (IR) and is used as a fourth parameter in Hansen solubility analyses.

Likewise, the parameters of a candidate fuel can be represented by a single point in the same space. To aid in discussion, the diagram in [Figure 1](#) is depicted in two dimensions in [Figure 2](#). In this figure, the green, red and blue points represent the 3D plot of the dispersive, polarity and H₂ bonding of three different fuels. The distance from the center of the solubility sphere to their respective location is their solubility distance (d_s). Fuels having solubility distance values much less than the interaction radius would be considered highly soluble, while those having distances greater than IR would have low solubility. Those lying on the surface of the sphere (or having similar values as IR) would be expected to exhibit modest to moderate solubility.

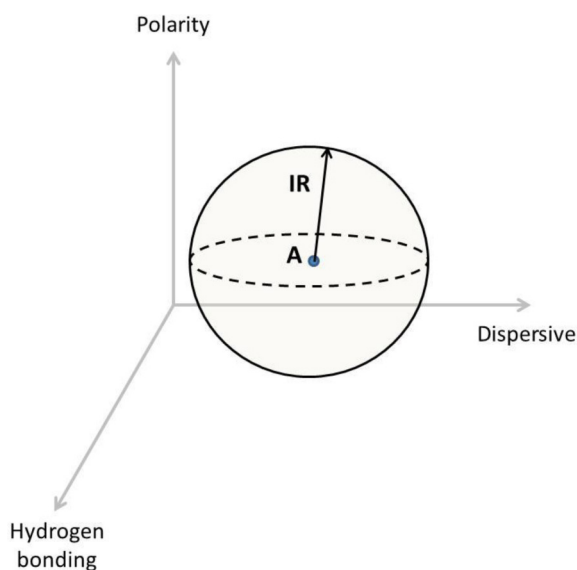


Figure 1. Diagram of solubility sphere used to represent Hansen solubility parameters.

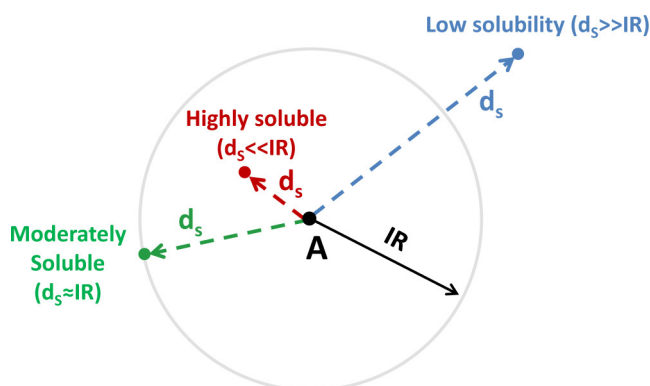


Figure 2. Two-dimensional representation of Hansen solubility sphere.

By subtracting the solubility distance (d_s) from the interaction radius (IR), one can get a measure of the **solubility potential** existing between the polymer and fuel, such that

- $IR - d_s$ values greater than $1 \text{ MPa}^{1/2}$ would be expected to exhibit high solubility,
- $IR - d_s$ values that are between $\pm 1 \text{ MPa}^{1/2}$ would be expected to have moderate solubility, and
- $IR - d_s$ values that are less than $-1 \text{ MPa}^{1/2}$ would be expected to have low solubility.

In this study the solubility potentials for the six elastomer materials were determined for the two baseline fuels representing gasoline and E10 (gasoline containing 10% ethanol) and the co-optima high-octane fuel candidates. In this study the Hansen solubility parameters for dodecane were used to represent gasoline. The parameters associated with dodecane have been determined to be good representatives of pump grade gasoline (as advised by the Hansen Solubility team) [14]. Similarly the parameters derived for E10, were based on dodecane containing 10% ethanol and the test fuel is denoted as E10D in this paper.

An example of the solubility potential results obtained for three elastomers and a fuel candidate blended with dodecane is shown in Figure 3. In many cases (especially for polymers exposed to alcohol blends) the solubility potential increases from the baseline values with the addition of the fuel candidate until a maximum is reached. Further additions then cause the solubility potential to decrease with increasing concentration. This effect is demonstrated for elastomers A, B and C shown in the figure. For elastomer A, the baseline solubility potential is around $1 \text{ MPa}^{1/2}$ indicating moderate solubility. However, the solubility potential rises rapidly with candidate concentrations up to a peak value of $4.2 \text{ MPa}^{1/2}$ associated with a blend content of 45%. At this concentration, high solubility is expected with elastomer A. However, when the concentration approaches 100% of the fuel candidate, the solubility potential drops to a level where moderate solubility is expected. Similarly, elastomer B exhibits high solubility with the neat baseline fuel which increases to a maximum of around $3.5 \text{ MPa}^{1/2}$ at 20%. Further additions of the candidate fuel produce a steep decline with concentration such that blends containing candidate levels greater than 70% would likely have low solubility. In contrast, elastomer C has low solubility potentials at 0 and 100% blend contents. However, concentrations approaching 50% would be expected to be moderately soluble based on the guidelines previously mentioned.

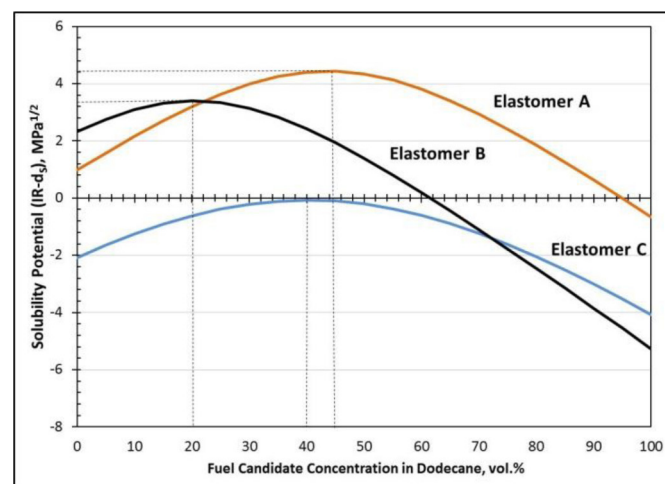


Figure 3. Example of solubility potential results for a hypothetical fuel candidate blend with dodecane and three elastomers.

It is important to note that not all polymers will exhibit a peak in solubility potential as shown in Figure 3. In some instances, the solubility increases or decreases linearly with concentration. In these cases maximum solubility occurs for the baseline fuel or neat fuel candidate.

CANDIDATE FUEL CHEMISTRIES

A listing of the thirty-four candidate fuels evaluated in this study along with their respective Hansen solubility parameters is shown in Table 1. All are pure compounds, except for the furanic mixture, which is a mix of two components. Also included in the table are the two baseline fuels, dodecane and E10D. These parameters were obtained from the HSPiP software package published by the Hansen solubility team [15]. This data set contains solubility parameters for over 10,000 chemicals.



As shown in Table 1 the candidate fuels are grouped according to their functional group. The alcohols contained a large number of candidates, and several of these, such as ethanol and isobutanol, have been extensively studied for their compatibility to fuel system elastomers and plastics [2,10–11]. Only one alkane and two alkenes are included in this study. The two aromatics are similar in structure and subsequently have nearly identical values for their Hansen solubility parameters. The esters had the largest number of identified

candidates. For this grouping the dispersive parameter values are somewhat similar for the eleven molecules, but variability exists in the values for the polarity and hydrogen bonding parameters. Three ether molecules were included along with a 60/40 blend of dimethylfuran and 2-methylfuran. The parameters for the furanic mixture were obtained using the rule of mixture approach which is considered applicable by Hansen [13]. Five ketones were also included in this study.

Table 1. Hansen solubility parameters used for fuel molecules in the solubility analysis. Parameters selected from *Hansen Solubility Parameters: A Users Handbook* [12]

CAS#	Fuel Candidates	Other Common Names	Hansen Solubility Parameters MPa ^{1/2}		
			Dispersive	Polarity	Hydrogen Bonding
	Baseline Fuels				
112-40-3	Dodecane (gasoline surrogate)		16	0	0
	E10D (E10 surrogate)		15.98	0.88	1.94
	Alcohols				
64-17-5	Ethanol		15.8	8.8	19.4
71-23-8	n-Propanol		16	6.8	17.4
67-63-0	2-Propanol		15.8	6.1	16.4
71-36-3	1-Butanol		16	5.7	15.8
78-92-2	2-Butanol		15.8	5.7	14.5
78-83-1	2-Methylpropan-1-ol	Isobutanol	15.1	5.7	15.9
137-32-6	2-Methylbutanol		15.3	4.7	13.5
115-18-4	3-Methyl-3-buten-2-ol		15.9	5.1	10.2
6032-29-7	2-Pentanol		15.6	6.4	13.3
	Alkanes				
540-84-1	2,2,4-Trimethylpentane	Iso-octane	14.1	0	0
	Alkenes				
107-39-1	2,4,4-Trimethylpent-1-ene	Iso-octene	14.7	1.1	1.4
3387-41-5	4-Methylene-1-(-methylethyl)bicyclo[3.1.0]hexane	Sabinene	16.6	1.5	1.8
	Aromatics				
25340-18-5	1,3,5-Triethylbenzene		18	0	0.6
108-67-8	1,3,5-Trimethylbenzene	Mesitylene	18	0.6	0.6
	Esters				
79-20-9	Acetic acid, methyl ester	Methyl acetate	15.5	7.2	7.6
141-78-6	Acetic acid, ethyl ester	Ethyl acetate	15.8	5.3	7.2
624-24-8	Pentanoic acid, methyl ester	Methylpentanoate	15	14.1	10.3
547-63-7	2-Methyl propanoic acid, methyl ester	Propionic acid, methyl ester (PAME)	14.7	5.3	12.4
868-57-5	2-Methyl butanoic acid, methyl ester	Methylbutanoate	15.8	5.2	6.5
105-54-4	2-Methyl butanoic acid, ethyl ester	Butanoic acid, ethyl ester (BAEE)	14.9	4.1	10.6
97-62-1	2-Methyl propanoic acid, ethyl ester	Ethyl propionate	15.5	6.1	4.9
108-212-4	Acetic acid, 1-methylmethyl ester	Isopropyl acetate	14.9	4.5	8.2
123-86-4	Acetic acid, butyl ester	Butyl acetate	15.8	3.7	6.3
123-92-2	Acetic acid, 3-methylbutyl ester	Isoamyl acetate	15.8	3.1	7
97-62-1	Ethyl 2-methylpropanoate		15.5	4.6	5.3
	Ethers				
100-66-3	Methoxybenzene		17.8	4.1	6.7
534-22-5	2-Methylfuran		17.3	2.8	7.4
625-86-5	2,5-Dimethylfuran		17.5	51	5.5
	Furanic mixture (60% dimethylfuran/40% 2-methylfuran)		17.42	4.18	6.26
	Ketones				
78-93-3	2-Butanone		16	9	5.1
107-87-9	2-Pentanone		15.3	6.1	4.1
96-22-0	3-Pentanone		15.8	7.6	4.7
64-67-1	2-Propanone	Acetone	15.5	10.4	7
120-92-3	Cyclopentanone		17.9	11.9	5.2

ELASTOMER MATERIALS

Polymers are grouped into three classes based on their internal structure and molecular network [16]. They include thermoplastics (often referred to as plastics), elastomers, and thermosetting resins (or thermosets). Thermoplastics are composed of linear or branched polymer chains, which will melt or soften with the application of heat. Elastomers (the subject of this study) contain polymer chains which, while crosslinked, can be readily deformed under stress, and when that stress is removed, they return to their original shape. Thermosets also contain crosslinking, but their molecular chains are rigid and more highly networked. Chain movement is restricted by the high degree of crosslinking in thermosets, and as a result, these materials degrade rather than become fluid (or soften) with increasing temperature. It is the ability to deform and subsequently return to their original shape, when stress is applied and removed, that makes elastomers ideal materials for sealing applications.

When considering elastomers (or any polymer for that matter), it is crucial not to view them as single homopolymer materials. They are almost always compounded with other polymers and additives. For example, acrylonitrile butadiene rubber (NBR), a common elastomer, is a co-polymer consisting of acrylonitrile and butadiene. In addition to co-polymer constituents, additives are also added to impart flexibility, oxidation resistance, and color (among other applications). It is quite possible that one (or more) of the additives is highly soluble, even though the primary polymer is not. These materials often make up a small percentage of the polymer mass, but provide important properties relative to the overall performance. If they are dissolved and extracted from the polymer structure, then the desired properties, especially durability, are also reduced or eliminated. Because the additive may be a small fraction of the overall polymer mass, its dissolution and extraction, may not be determined by volume swell measurements alone. The extent to which these additives are solvated and extracted by fuel can also be assessed via solubility analysis. Unfortunately, most manufacturers do not provide precise information on additive packages for elastomer and plastics materials, and therefore these components were not included in this study.

For polymers it is more challenging to obtain accurate Hansen solubility parameters than for single component fuels. The primary reason is that processing and additives play a significant role in polymer performance. And it is difficult to obtain accurate information from manufacturers since this information tends to be proprietary. Earlier solubility efforts by ORNL were able to identify representative Hansen solubility parameters through a trial-and-error approach based on volume swell measurements [10–11]. These parameters are listed in Table 2, which also includes the interaction radius for each elastomer type. The elastomer materials evaluated in this study include fluorocarbon, acrylonitrile butadiene rubber (NBR), styrene butadiene rubber (SBR), neoprene, polyurethane, and silicone rubber. A list of these materials with their applications is also included in Table 3.

Of these, NBRs are the most ubiquitous due to their low cost and combination of strength and pliability. NBR exists as copolymer of acrylonitrile and butadiene, and its mechanical properties can be controlled by varying the level of each component to meet a

particular application. Prior exposure studies have been performed on six grades of NBR ranging from 66% to 70.2% fluorine [11]. The results from these studies have shown that although co-polymer and fluorine contents were different for each grade, the swelling behavior of automotive and small engine grades were similar and could be approximated using the parameters listed in Table 2 for each type of NBR. SBR is a copolymer of styrene and butadiene and is similar in structure to NBR. However, it has been shown to swell to higher levels when exposed to gasoline, oxygenates, and diesel fuel. Neoprene is also used in sealing applications (albeit less than NBR). Its compatibility performance has been found to roughly match that of NBR. Studies on silicone have shown that it undergoes extremely high swelling (relative to other elastomers) when exposed to gasoline and oxygenated fuels, but, when dried, it returns to its original volume [10–11].

Table 2. Hansen solubility parameters and interaction radii for elastomers used in the solubility analysis. Parameters selected from *Hansen Solubility Parameters: A Users Handbook* [13]

Elastomer Type	Hansen Solubility Parameters, MPa ^{1/2}			Interaction Radius, MPa ^{1/2}
	Dispersive	Polarity	Hydrogen	
Fluorocarbon	14.6	10.0	1.6	8.8
NBR	17.8	3.2	3.4	7.3
Neoprene	18.1	4.3	6.7	8.9
Polyurethane	18.1	9.3	4.5	8.0
SBR	17.2	6.0	4.6	7.3
Silicone	13.8	5.0	1.2	14.3

Table 3. Listing of elastomer materials and their primary application in fueling systems.

Material type	ASTM Nomenclature	Application
Fluorocarbon	FKM	Seals (o-rings, gaskets, etc.)
Acrylonitrile-butadiene rubber	NBR	Seals (o-rings, gaskets, etc.) Fuel hoses
Polyurethane	PU	Coatings
Neoprene	CR	Seals (o-rings, gaskets, etc.) Fuel hoses
Styrene-butadiene rubber	SBR	Fuel hose cover
Silicone	VMQ	Seals (o-rings, gaskets, etc.)

Fluorocarbons are classified as high performance elastomers and have demonstrated excellent compatibility with many fuel types. Studies have shown that the performance of eight automotive and fuel grades (includes FKM types 1 and 2) have similar compatibilities with gasoline and oxygenated fuels [11]. They are, however, incompatible with some ketones, especially acetone [3, 4, 5, 6, 7, 16]. The Hansen solubility parameters listed in Table 2 have been found to correspond well to the observed physical swelling in various fuel chemistries. In contrast to the other elastomers included in this study, fluorocarbons typically retain fluid after drying. This retention results in a small volume increase after drying from their original values. Fluorosilicone rubbers are also common fuel system elastomers and the compatibility properties of a general purpose grade (LM115) were found to be comparable to fluorocarbons in gasoline test fuels and oxygenates. Unfortunately, the data on solubility parameters for fluorosilicone (and its grades) are not widely available. The values obtained from literature

sources, or otherwise calculated, have not corresponded with the observed volume changes exhibited in empirical studies. As a result, fluorosilicone was not included in this study.

Polyurethane is different from the other elastomer types in that its use is primarily restricted to coatings, and not as seals or in hoses. These elastomers have been investigated empirically, and their volume swell behavior in these investigations was found to correspond well with their predicted solubilities using the Hansen approach. This correlation was observed in test fuels representing diesel, gasoline, and also fuels composed of gasoline blended with ethanol or isobutanol [2,10–11]. As a result, there is some prior confidence in the empirical performance matching their solubility potential with known test fuels. A listing of the six elastomer types with their respective Hansen solubility parameters and interaction radii is shown in Table 3.

The solubility potential ($IR-d_p$) curves for each candidate fuel with the six elastomers are shown in the Appendix as a function of blend content with dodecane and E10D. For many of the fuel candidates, the maximum solubility potential occurs for mixture with either of the baseline fuels, rather than for the neat candidate or baseline fuel. Exceptions are the alkanes, alkenes, and aromatics which show a more linear relationship with concentration and, consequently, maximum solubility potential occurs for the neat candidate or baseline fuel. Comparison of the solubility curves for each baseline fuel has shown that the chemistry of the base fuel has little overall impact on the solubility curves. The only discernable difference is that the location of maximum solubility potential shifts to slightly lower blend concentrations when moving from dodecane to E10D, and the solubility potential is slightly increased for fuel candidate concentrations less than 50%.

The resulting data presented in this section were derived from the curves listed in the Appendix. To better facilitate discussion and analysis, results for each molecular class of the candidate fuels are discussed separately. In each grouping the two baseline fuels are included in the solubility charts for comparison. The solubility potentials were determined for each candidate and baseline fuel chemistry, and elastomer type. Additional data are included to show the solubility behavior of the fuel candidate with E10D. This data consists of bar charts showing the maximum value of the solubility potential for each blend and the corresponding candidate concentration associated with these maximum values.

RESULTS

Alcohol Candidate Fuels

For each elastomer type, the solubility potential was determined for each alcohol. These results are shown in Figure 4 along with the two baseline fuels. For silicone and SBR, the solubility performances of dodecane and E10D were similar, but for the other elastomer types, higher solubility is expected with the addition of 10% ethanol. This observation has also been confirmed in earlier empirical studies

[2,10]. In general, the results for the alcohol candidates show improved compatibility with the six elastomer types compared to the two baseline fuels. The primary exception is 2-methyl butanol, which showed significantly higher solubility with neoprene than the baseline fuels. This alcohol exhibited the highest solubility of the alcohols with the other elastomer materials, although the solubility was still significantly below the values for the base fuels.

Compared to the two baseline fuels, the candidate alcohols show much lower solubility potential for silicone rubber. For many gasoline fuel systems, silicone is not widely utilized due to its high solubility with both gasoline and E10. If the alcohols were to be used as a neat fuel, then silicone offers a low cost alternative. In practice, these alcohols are likely to exist as low-level blends with gasoline or E10, and, at these concentrations, silicone will not be suitable for many applications. Of the alcohols evaluated, 2-methyl-butanol shows the highest solubility potential (and therefore potentially least compatible) for each of the elastomer types.

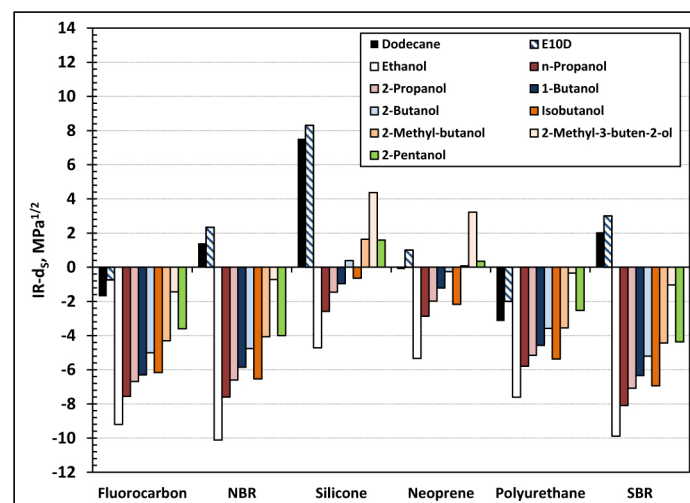


Figure 4. Solubility potential of the alcohol candidate fuels with key fueling elastomer materials.

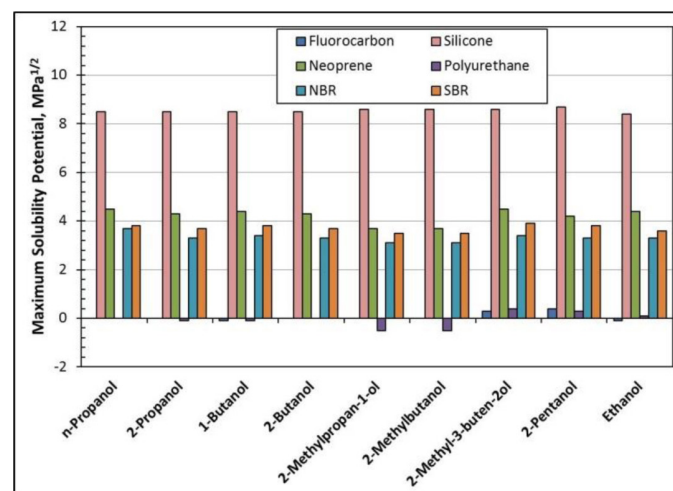


Figure 5. Maximum solubility potential of the alcohol candidates for each elastomer when blended with E10D.

The charts in Figures 5 and 6 show the potential solubility results for the alcohol candidate fuels when blended with E10D. (Ethanol results were for blends of dodecane since E10D already contains ethanol.) As shown in Figure 5, the maximum solubility potential for silicone rubber is extremely high for blends containing 10 to 20% of the alcohol type, regardless of the specific chemistry. These results show that while silicone has low solubility with the neat alcohols, it becomes highly soluble when low levels are blended with dodecane (or E10D). In contrast to silicone, fluorocarbon and polyurethane are expected to exhibit low-to-modest solubility for each of the alcohol candidates.

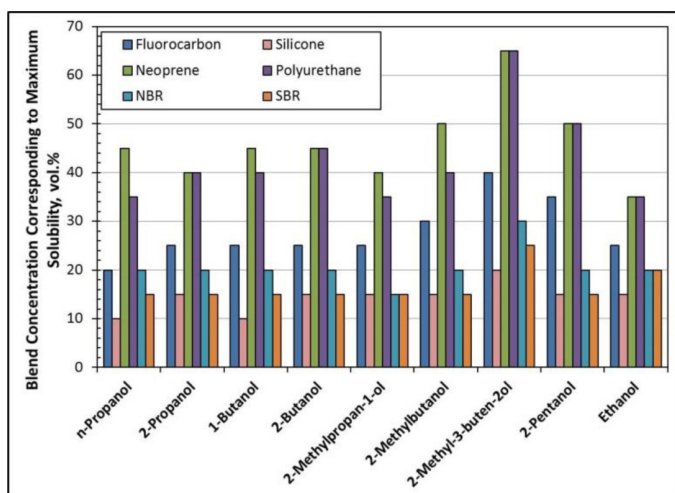


Figure 6. Alcohol concentration corresponding to the maximum solubility for each elastomer. Baseline fuel is E10D, except for ethanol which is blended with dodecane.

The remaining elastomers (neoprene, NBR and SBR) have relatively high solubility potentials even though their maximum values are half that of silicone. Moderate to high swelling is predicted for these elastomers. For NBR and SBR, maximum swelling occurs at relatively low blend levels (15-20%), while for neoprene, maximum solubility is expected for alcohol concentrations approaching 40%.

Alkane, Alkene and Aromatic Candidate Fuels

The results for the alkanes, alkenes and aromatic fuel candidates are shown collectively in Figures 7–9. Comparison of the neat candidate fuel results in Figure 7 indicates that fluorocarbons would have low to moderate solubility with no discernable difference from the two baseline fuels for any of the six elastomers evaluated in this study.

Low solubility (good compatibility) is also expected for polyurethane. The results for NBR are mixed; the alkane fuel molecule showed low solubility potential for these elastomers, while the alkenes and aromatic candidates produced solubility potentials similar to E10D. Interestingly, the addition of 10% ethanol significantly raises the solubility potential of dodecane for NBR. SBR exhibited similar performance to NBR with two notable differences; the solubility potentials for the two baseline fuels are similar and the solubility potentials for the alkene and two aromatics are significantly

higher than the baseline fuels. As a result SBR may experience less compatibility with these fuel types. For silicone, 2,2,4-trimethylpentane, iso-octene, and sabinene exhibit compatibility results similar to the baseline fuels, while the two aromatics show improved compatibility performance compared to the baseline fuels. Neoprene is expected to have improved compatibility performance with 2,2,4-trimethylpentane. For this material the solubility potential of iso-octene is similar to that of dodecane, and thus similar compatibilities are expected. The other candidate fuels in this grouping would be expected to exhibit similar solubility potential (and therefore compatibility) to the E10D baseline. SBR shows good solubility potential with both 2,2,4-trimethylpentane and iso-octene compared to the baseline fuels, but high solubility is expected with sabinene and the two aromatics. While SBR may not be compatible with sabinene and the aromatic candidates, the remaining elastomers should exhibit acceptable compatibilities with these fuel types. Interestingly, the alkane molecule, 2,2,4-trimethylpentane (also known as iso-octane) showed the best potential compatibility of the fuel types with the elastomers, with the sole exception being silicone rubber where it showed slightly higher solubility potential than the baseline fuels.

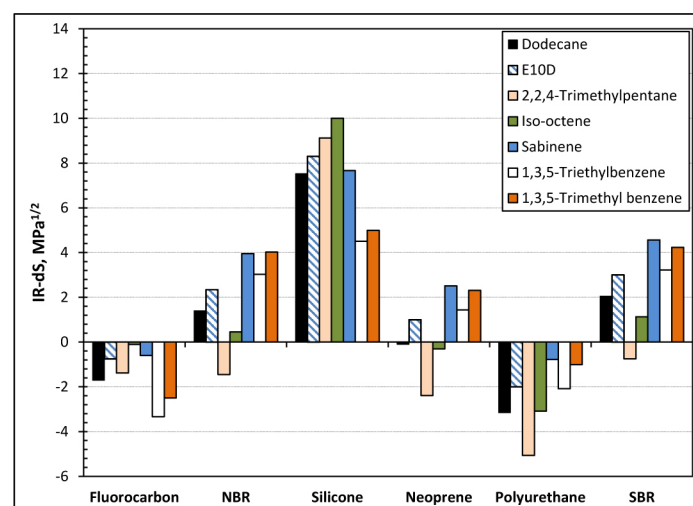


Figure 7. Solubility potential of the alkane, alkenes, and aromatic candidate fuels with key fueling elastomer materials.

The solubility behavior for the alkane, alkenes and aromatics when blended with E10D (or dodecane) differed markedly from the alcohols and other fuel chemistries in that there was no pronounced maximum solubility potential observed for blended fuel mixtures (Figures A.10 to A.14 in Appendix). When blended with E10D, the solubility potential results generally increased or decreased in a roughly linear manner from 0 to 100% of the fuel candidate. The actual direction depended on the fuel type. However, in some cases, a slight maximum value was observed. The results for these fuel candidate blends are shown in Figures 8 and 9. The results for fluorocarbon show that modest solubility is expected for each candidate and blend content. Interestingly, for this material, peak solubility occurs at high levels of iso-octene and sabinene. Otherwise the baseline fuel produces the highest solubility potential.

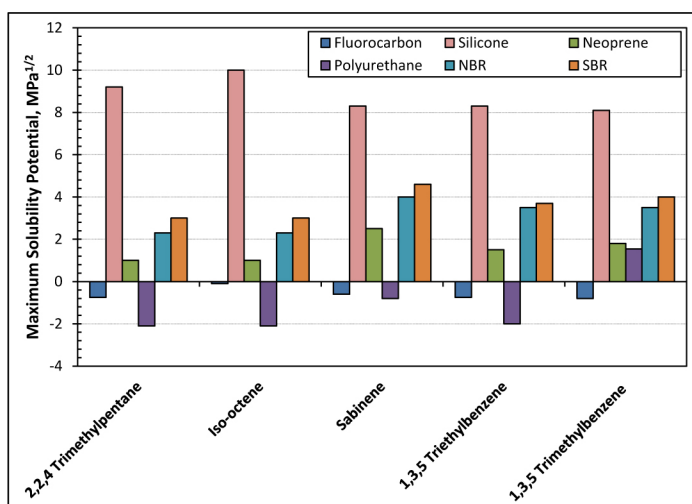


Figure 8. Maximum solubility potential of the alkane, alkene, and aromatic candidate fuels when blended with E10D for each elastomer.

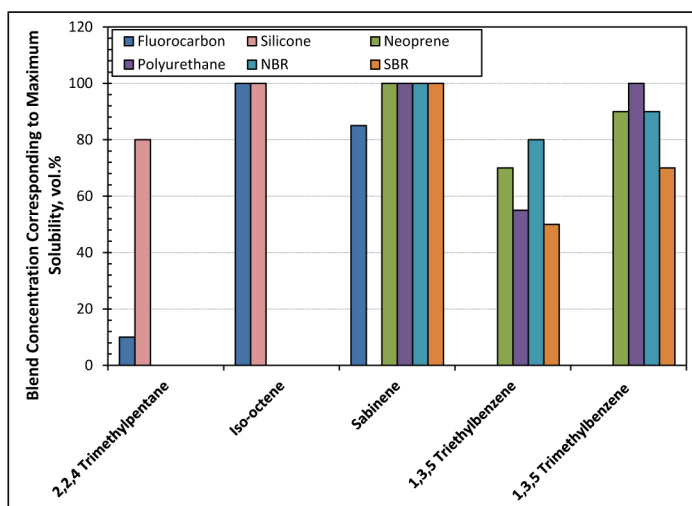


Figure 9. Alkane, alkenes and aromatic concentration corresponding to maximum solubility for each elastomer for candidate fuels blended with E10D.

For silicone, both 2,2,4-trimethylpentane and iso-octene produce high solubility potentials at high blend levels, which is interesting since the solubility of silicone is usually highest for the baseline fuel. As can be seen in Figure 9, neat sabinene produces maximum solubility for neoprene, polyurethane, NBR and SBR. Similar behavior is also noted for the two aromatics.

Ester Candidate Fuels

The results for the neat esters and two baseline fuels are shown in Figure 10. The most compatible neat ester molecules were methylpentanoate, PAME and BAME. These three fuel candidates exhibited low solubility potentials with fluorocarbon, NBR, polyurethane and SBR. Higher solubility potentials were noted for silicone and neoprene; however these values are significantly lower than those determined for the baseline fuels and would be deemed

compatible with these two elastomer types. The other ester candidates produced results which varied depending on the candidate fuel chemistry and elastomer type in question.

For fluorocarbon, the isopropyl acetate, butyl acetate, and isoamyl acetate molecules all show modest solubilities, similar in value to the E10D baseline fuel. Moderately higher solubilities are expected with methyl acetate, ethyl acetate, methylbutanoate, ethyl propionate, and ethyl 2-methylpropanoate. The relatively higher solubility potentials of ethyl propionate and ethyl 2-methylpropanoate may preclude fluorocarbon use with these candidate fuels. In contrast the solubility potentials for the candidate fuels with NBR are less than the value obtained for E10D. This result suggests that the candidate fuels will be compatible with existing NBRs for fueling applications. For SBR the candidate fuels produce solubilities either similar to, or lower than, the baseline fuels and would, therefore, be considered compatible with this elastomer type. The baseline fuels produced high solubility results for silicone and the candidate fuels exhibited similar or reduced solubility. These high solubilities preclude use of the baseline fuels and many ester candidates with silicone. Methylpentanoate, however, exhibits only moderate solubility with silicone, and therefore silicone may be suitable for use with neat methylpentanoate in some applications.

Neoprene showed significantly higher solubility (compared to the baseline fuels) for ethyl acetate, methylbutanoate, butyl acetate, and possibly ethyl 2-methylpropanoate. As a result, neoprene may not be suitable for use with any of these three fuel candidates. The solubility potentials for methyl acetate, ethyl propionate, and isoamyl acetate are also higher than the baseline fuel E10D, but probably not at a level that would cause a concern.

For polyurethane elastomers, methyl acetate, ethyl propionate, methylbutanoate, and ethyl 2-methylpropanoate all show a pronounced increase in solubility relative to the baseline fuels. While the solubility potentials for these fuel candidates are not as high as they are for silicone and neoprene, they may be high enough to warrant replacement of polyurethane seals and coatings for certain applications.

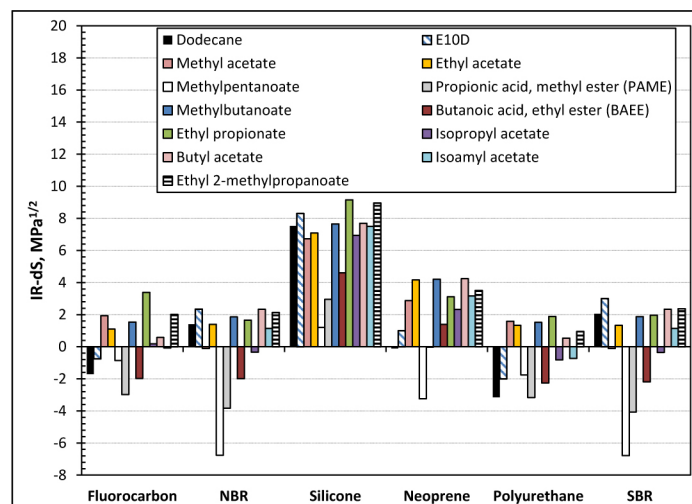


Figure 10. Solubility potential of the ester candidate fuels with key fueling elastomer materials.