

Compatibility of Dimethyl Ether (DME) and Diesel Blends with Fuel System Polymers: A Hansen Solubility Analysis Approach

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ABSTRACT

The compatibility of notable infrastructure elastomers and plastics with DME and its blends with diesel fuel were examined using solubility analysis. The elastomer materials were fluorocarbon, acrylonitrile butadiene rubber (NBR), styrene butadiene (SBR), neoprene, polyurethane and silicone. Plastic materials included polyphenylene sulfide (PPS), polyethylene terephthalate (PET), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyoxymethylene (POM), polybutylene terephthalate (PBT), polypropylene (PP), high density polyethylene (HDPE), along with several nylon grades and thermosetting resins. These materials have been rigorously studied with other fuel types, and their volume change results were found to correspond well with their predicted solubility levels.

A Hansen solubility analysis was performed for each material with DME, diesel, and blends of both fuel components. The results for the elastomers indicate that DME and its blends with diesel fuel will offer improved compatibility with NBR and SBR materials. Silicone, neoprene and polyurethane show similar solubility potential for any combination of DME and diesel, so no degradation is expected with DME. In contrast, fluorocarbon can be expected to become increasingly incompatible with increased DME concentration. In general, the solubility analysis also indicated that many of the plastic materials can be expected to have good to excellent compatibility with DME and its blends with diesel fuel. The analysis also indicated that polyester resins should exhibit high solubility (and therefore high swelling) in both diesel and DME. However, previous empirical results showed that this result was not an accurate reflection of polyester resin performance in diesel fuel.

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INTRODUCTION

Background

The increasing production and availability of abundant natural gas resources offers a means of lowering energy costs while also reducing our overall reliance on foreign energy imports. Natural gas, by itself, has significant utility as an energy fuel, not only because it is domestically abundant but also because it does not produce high hydrocarbon and soot emissions when combusted [1]. However, its use as a transportation fuel has been limited due to its low energy density relative to gasoline and diesel. Even when liquefied, its low specific energy density means that tanks must be roughly ten times the size of gasoline tanks to get equivalent mileage. Another way to utilize this abundant resource is to convert it to methanol or dimethyl ether, both of which have much higher energy density than natural gas. Natural gas can be readily converted to methanol and run in spark-ignited (SI) engines and this approach is being pursued in some countries. Methanol has several advantages as a liquid fuel, especially its miscibility with gasoline and diesel fuels, but it has one key disadvantage in that it has numerous compatibility problems [2]. Methanol (like ethanol) adsorbs water which can be corrosive to many metal-based systems and components. The combustion of

methanol produces acids, which subsequently accelerate the wear and corrosion of valves, valve seats and other in-cylinder components. Another unattractive feature of methanol is its ability to absorb water, which can reduce the fuel heating value and phase-separate causing aqueous-based corrosion. The energy density of methanol relative to gasoline and diesel is shown in [Table 1](#).

Table 1. Energy densities for selected fuels.

Fuel Type	Energy Density (MJ/L)
Diesel Fuel	35.6
Gasoline	32.4
Methanol	15.6
Dimethyl Ether	19.1

Dimethyl ether (also shown in [Table 1](#)) can readily be produced via methanol dehydration, and it can also be synthesized from syngas (CO and H₂) [3, 4, 5]. It has the advantage in that it can be readily produced from various feedstocks, but most commonly from coal and natural gas. Physically DME is a gas at most ambient conditions, but it has a much higher energy density than either natural gas or methanol (when liquefied). There have been many studies regarding evaluating DME properties during combustion in compression

Table 2. Compatibility ratings for common seal materials according to manufacturer.

Material Class	Company Name				
	Mykin	Geotech	Hargraves	Allorings	Parr
Elastomers					
NBR & SBR	Satisfactory	Acceptable		Not recommended	Acceptable
Neoprene	Doubtful	Unsatisfactory			
Fluorocarbon	Fair		Acceptable	Not recommended	Acceptable
Fluorosilicone			Acceptable	Recommended	Acceptable
Silicone				Recommended	Acceptable
Plastics					
PTFE (Teflon™)		Resistant			

ignition engines. DME has excellent combustion characteristics due to its high cetane number, and very low emissions of soot and hydrocarbon are produced. Unlike methanol, DME does not produce acids when combusted. DME is fully miscible with diesel fuel, and studies have shown that its vapor pressure is reduced by a small amount when in solution with diesel fuel [6, 7, 8].

While the compatibility of most petroleum and bio fuels with fueling infrastructure materials is well understood, the compatibility of DME with infrastructure materials, especially polymers has not been well studied [4]. Because DME does not readily break down into acids, as is the case with ethanol and butanol, it can be expected to be compatible with most metals and alloys. However, it is possible that DME is soluble with one of more key infrastructure polymers that are used ubiquitously as hoses, seals, tanks, valves, and piping components which are used in fuel handling infrastructure or onboard fuel delivery systems. This unknown was pointed out as a research need by one study [4].

Compatibility Ratings for Polymers

A literature survey quickly reveals that compatibility data for dimethyl ether with elastomer and plastics is limited. Several rubber seal and component suppliers do provide some limited compatibility data with their products and DME [9, 10, 11, 12, 13]. Unfortunately, the data provided by the seal and plastic manufactures are expressed as relative rankings usually from a scale of 1 to 4, with 1 representing excellent compatibility and 4 denoting incompatibility. Unfortunately the terminology used by many manufacturers is inconsistent and vague. For instance, some companies describe compatibility as either “satisfactory” while others used the term “acceptable”. Likewise, poor compatibility is described as “unsatisfactory” or “not recommended” depending on the manufacturer or supplier. These relative compatibility descriptors are listed in Table 2 for five seal and plastic manufacturers [9, 10, 11, 12, 13]. It is important to note that number of polymers listed is very short and does not include many that are, in fact, commonly used in existing infrastructure systems.

As shown in the table, the list of materials rated for compatibility is very limited and the list varies dramatically according to manufacturer. Important elastomers such as polyurethane were not included, nor were many commonly used plastic materials, such as PET, PVDF, nylon, polyethylene, acetal (also known as POM) and polypropylene. Interestingly, NBRs (which are common hose and seal materials) are rated as compatible for three manufacturers, but one company (Allorings) does not recommend NBR for use with

DME. Similar conflicting results are also noted for fluorocarbon as well. It is important to note that the compatibility ratings listed in Table 2 are for exposure to neat DME only. Therefore, these tables cannot be used to assess compatibility of blends of DME and other chemicals or fuel types. The reason is that the solubility of the fuel blend is often significantly influenced by each fuel component and its concentration. For some multi-component fuels (such as ethanol blended gasoline), the fuel blend is often more soluble than each individual constituent. When considering the results in Table 2, it is important to know that these are very crude guidelines. The performance will vary according to the application and for some applications, a poor ranking may, in fact, be acceptable.

Solubility

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). It can also mean susceptibility to chemical attack, although most polymers evaluated in this study are not considered to be chemically reactive to diesel fuel or DME. (One possible exception is polyurethane, which has been shown to be reactive to some oxygenates.) [14, 15, 16] If a polymer is completely insoluble with the fuel, then it will be physically unaffected when exposed to the fuel. However, at the other extreme, if a polymer is completely soluble (or miscible) with the fuel, then it will be completely dissolved by the fluid. In reality most polymers are partially soluble with most fuels, and this solubility manifests itself as volume swell of the polymer, the extent of which corresponds to the degree of 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. 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. This approach is based on the Flory-Huggins solution theory [17].

Fuels and elastomers having similar solubility parameters will have a higher affinity for permeation and dissolution than those with dissimilar values. This relationship serves as the basis for the phrase “like dissolves like”. 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 due to dispersion (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, its results are still an approximation. 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 [17].

Solubility-based analysis studies are important because they can be used to quickly identify fuel blend concentrations and polymer materials most susceptible to leakage without having to perform a broad (and time consuming) empirical study. In this paper, a Hansen solubility analysis was performed for common fuel systems elastomers for blends of diesel and DME. The results from this study can be used to guide the selection of elastomers for use with DME-diesel fuel blends. The relationship of between solubility and blend chemistry is also useful for determining which fuel blend levels are the most (or least) compatible.

Another important consideration is that many elastomers and plastics are, in fact, complex compositions of one or more polymer components, and often include low molecular weight additives such as oligomers, plasticizers, stabilizers, lubricants, or other flexing agents. The extent to which these additives are solvated and extracted by fuel can also be assessed via solubility analysis. However, 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.

MATERIALS AND METHODOLOGY

Materials

The two polymer classes evaluated in this study include elastomers and plastics. From each of these two classes, specific types and grades were selected that are common to fuel storage and delivery systems. These materials have been investigated empirically in several studies by the lead author (and others), and their volume swell behavior was found to correspond 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 [14, 15, 16, 18, 19]. As a result, there is some prior confidence in the empirical performance matching their solubility potential with known test fuels. However, it is important to note that in a recent study by Heitzig et al. [20], this correlation was not observed for some elastomers.

Elastomers

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 shown 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. SBR is a copolymer of styrene and butadiene and is similar 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 roughly matches that of NBR [14, 15, 16].

Table 3. Summary of elastomer materials and their application.

Material type	Application
Fluorocarbon	Seals (o-rings, gaskets, etc.)
Fluorosilicone	Seals (o-rings, gaskets, etc.)
NBR	Seals (o-rings, gaskets, etc.) Fuel hoses
Polyurethane	Coatings
Neoprene	Seals (o-rings, gaskets, etc.) Fuel hoses
SBR	Fuel hose cover
Silicone	Seals (o-rings, gaskets, etc.)

Studies on silicone have shown that it undergoes extremely high swelling (relative to other elastomers) when exposed to gasoline and diesel fuels, but, when dried, it returns to its original volume. Fluorocarbons are classified as high performance elastomers and have demonstrated excellent compatibility with many fuel types. They are, however, incompatible with ketones, especially acetone [18]. 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. Polyurethane is different from the other elastomer types in that its use is primarily restricted to coatings, and not as seals or in hoses. Prior studies have shown that polyurethane will chemically degrade with gasoline containing ethanol [14].

Plastics

As with the elastomers, the plastic materials included in this study have been extensively studied for their compatibility properties with test fuels representing gasoline, ethanol and isobutanol blends (with gasoline), and diesel. Most of these materials also showed good correspondence between their predictive relative solubility and volume swell measurements. In general most plastics are used as structural components as is the case for flexible and rigid piping. However, some plastics, such as nylon and polytetrafluoroethylene (PTFE or Teflon™) are used as o-rings and other seals. Other uses include permeation barriers, especially for those plastics which exhibit excellent resistance to permeation.

Plastic materials are divided into two subclasses: thermoplastics and thermosets (or thermosetting resins). Thermoplastic polymers do not undergo a chemical change in composition when heated, though they do soften or melt. When cooled they typically return to their original composition, and consequently, they can be molded repeatedly. Thermosets, on the other hand, can only be cured and shaped once. After forming, they remain in a solid (highly rigid) state and cannot be melted. In the thermosetting process, the chemical reaction forming the cross-linked polymer is not reversible. A complete listing of the plastic materials according to type and application is shown in [Table 4](#).