



Full Length Article

Influence of biodiesel decomposition chemistry on elastomer compatibility

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ABSTRACT

The compatibility of biodiesel blends with five common elastomers (acrylonitrile rubber or NBR, fluorocarbon, neoprene, ethylene propylene diene monomer or EPDM, and silicone) was assessed using Hansen solubility parameters. A solubility analysis was performed over the full diesel blend range and the model used methyl hydroperoxide, acetaldehyde, and formic acid to represent the decomposition products of biodiesel. An empirical study was also conducted to determine the efficacy of the approach to predict the volume swell of elastomers. This study included the influence of biodiesel with acetaldehyde and formic acid. The solubility model showed good agreement with measured volumes for fluorocarbon, neoprene, EPDM, and silicone. However, solubility curves for NBR did not reflect the measured volume changes, and therefore the solubility parameters used for NBR in this study are not considered reliable. The results showed that formic acid caused higher swelling in NBR, fluorocarbon, neoprene, and silicone than did acetaldehyde. For EPDM, the measured volume decreased with both biodiesel concentration and the addition of formic acid.

1. Introduction

Biofuels are used as transportation fuels to improve greenhouse gas reduction and to lessen dependency on fossil fuels. One of the more established biofuels is biodiesel, which is typically blended with diesel in levels of 5% (B5), 10% (B10) or 20% (B20) by volume. Biodiesel consists of fatty acid methyl esters (FAMES) which are derived via transesterification of vegetable oils or animal fats. Vegetable feedstocks include soybean, rapeseed, palm and camelina, but it can also be derived from tallow. The resulting FAME profiles are different for each feedstock, but the FAME molecular structures are similar. As a result, many of the physical and chemical properties are also similar. The methyl ester groups which make up biodiesel are known to be more polar than petroleum diesel. As a result, biodiesel is likely to cause higher swelling in polymers, many of which have moderate-to-high polarity. For polymers compatibility generally refers to the level of swelling induced by the fluid (or solvent). Because polymers, especially elastomers, are used ubiquitously in fuel storage and dispensing systems as hoses and seals, it is important to understand their compatibility with fuel chemistries to prevent failure and leakage.

Several studies have evaluated the impact of biodiesel and its blends with diesel on elastomeric materials [1–16]. A review was provided by Haseeb et al. [17], who pointed out that the interactions of biodiesel with polymeric materials are complex and not entirely understood.

Many of these studies were concerned primarily with acrylonitrile butadiene rubbers (NBRs) and fluorocarbons, since these two materials are prevalent in fueling systems. The compatible nature of fluorocarbon with unaged biodiesel (i.e. low volume swell) has been confirmed in several studies [1,3,5–14]. However, for NBR, the performances were more varied depending on the study and blend level. Modest (0–10%) mass or volume increases in NBR were reported in several studies [1,6,9,11,13,14]. Haseeb et al. [3] also reported low volume expansions, but only for low blend levels (less than B20); for B100, they recorded a mass increase near 15%. Exceptionally high mass increases of 40% and 50% were reported by Tongroon et al. [8] for B0 and B20, respectively. In this case, the high mass gain associated with B0 suggests a highly aromatic diesel and/or a highly incompatible grade of NBR.

For those investigations that evaluated performances over the full blend range, the observed mass/volume increase was reported to be roughly linear from B0 to B100 by Alves et al. [1] and Haseeb et al. [3]. However, Butcher et al. [13] observed higher swelling at lower blend levels than for B100. This result contradicts those reporting increased swell with increasing biodiesel concentration over the full blend range. Possible reasons for these reported differences in swell behavior are attributed to varying aromatic levels of the diesel, the wide compositional range and fabrication methods of NBRs, and the quality of the biodiesel. Exposure studies with biodiesel require extensive exposure

Abbreviations: ACN, acrylonitrile; EPDM, ethylene propylene diene monomer; FAME, fatty acid methyl ester; HSP, Hansen solubility parameter; NBR, acrylonitrile butadiene rubber; RED, relative energy difference; RME, rapeseed methyl ester; SME, soybean methyl ester; r_1 , interaction radius; d_s , solubility distance

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periods and are usually conducted at elevated temperatures; these conditions promote fuel degradation. As a result, it is highly likely that the chemistry of the biodiesel is changing during the exposure period, and these chemical changes further complicate interpretation.

Silicone, chloroprene (or neoprene), and ethylene propene diene monomer (EPDM) have also been evaluated (albeit to a lesser extent than NBR and fluorocarbon) for their compatibility with biodiesel. EPDM has been shown to exhibit substantially high swelling with biodiesel, but exposure to neat diesel results in even higher volume increases [6,7,15]. This behavior was attributed to the nonpolar nature of EPDM, which increases its affinity to the less polar diesel. The few studies that have evaluated chloroprene [8,15] show significantly higher mass/volume increases in biodiesel and its blends. The reported swelling was higher than for NBR exposed to the same conditions. Silicone was also evaluated in several biodiesel types and shown to exhibit modest (10–20%) swelling in most instances [15].

The degradation of biodiesel has been the subject of several studies [18–20]. Decomposition of the fatty acid methyl esters is complex and involves multiple mechanisms. The initial degradation reaction is the formation of hydroperoxides as FAMES react with oxygen. The alpha carbon positions on methyl ester chains are highly susceptible to hydrogen abstraction via radicals. An oxygen molecule then attaches to the alpha carbon and subsequently draws a hydrogen molecule away from another methyl ester to form a hydroperoxide. This reaction is self-propagating, and can form rapidly for some methyl ester groups [19]. The O-O-H end group is highly reactive due to the large hydrogen bonding force arising from the electronegative oxygen atoms and it has high polarity emanating from the asymmetry of the peroxide structure which causes unequal sharing of valence electrons. A secondary reaction involves the breakdown of these hydroperoxides into aldehydes, which further decompose into carboxylic acids (and to a lesser amount ketones and alkenes) [1]. Further reactions involve the production of oligomeric and polymeric structures [20].

The oxidation of biodiesel is known to negatively impact the physical properties of the fuel and tests have been devised to measure the levels of peroxides and acids to determine the level of degradation [20]. Understanding how the solubility of biodiesel is influenced by degradation products is essential in assessing polymer compatibility, especially for those elastomers and plastics used to handle, store and dispense biodiesel and its blends. Thomas et al. [5] evaluated the effects of aging on biodiesel composed of rapeseed methyl ester (RME) with fluoroelastomers and found that volume swell increased dramatically with aging time. However, they noted conflicting results for RME biodiesel containing minor levels of water. Studies performed by Butcher et al. [13] on NBR showed a strong correlation between total acid number and the observed swell of NBR in B100. These studies indicate the importance of degradation products on the solubility, which appears to be important even at relatively low blend levels.

The primary degradation products of biodiesel are well known and each of these products has solubility characteristics different from the FAMES comprising biodiesel. To ascertain the effects of biodiesel degradation on elastomer compatibility, a study was conducted using Hansen solubility parameters (HSPs) to evaluate the solubility potential of five common elastomers with a representative biodiesel containing various levels of hydroperoxide, aldehyde, and formic acid. Since solubility is roughly proportional to volume swell, the analysis gives insight into the effects of each degradation product and blend level. These analyses were performed over the full blend range with a typical on-highway diesel fuel. This approach has proven useful in predicting and explaining compatibility phenomena observed in other polymer-fuel combinations [21–23]. However, a key limitation is that for some

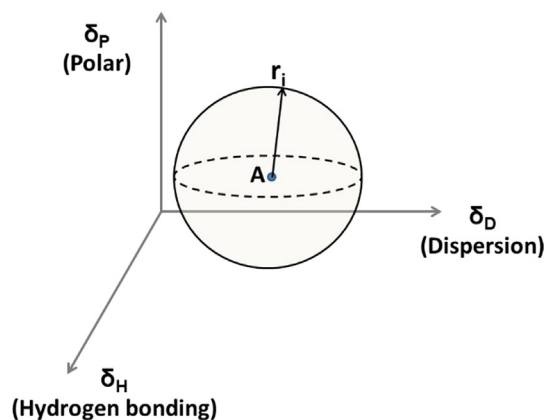


Fig. 1. Diagram of solubility sphere used to represent Hansen solubility parameters.

elastomers, especially those which are heavily compounded, such as NBR and neoprene, the existing solubility parameters may not be representative of the grade being evaluated.

2. Solubility and Hansen solubility parameters (HSPs)

Solubility analysis is based on the weak binding forces that promote permeation and dissolution. Mutual solubility is based on the degree of similarity (affinity) of these binding forces that exist between the solute and solvent. In this study the solute is the elastomer (which is a solid) and the solvent is the fuel. Solubility analyses assign parameters to both the solute and solvent to represent these attractions, whereby solubility is proportional to the degree of similarity of these parameters to each other. For each material and fluid, the Hansen solubility parameters (HSPs) method assigns a parameter to cohesive forces associated with atomic dispersion (δ_D), polarity (δ_P), and hydrogen bonding (δ_H) to represent the total cohesive energy density which is the sum of the square of these three attractive forces [24].

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (1)$$

Compounds having similar HSPs will have similar attractive affinities. For solutes, these three parameters define the location of a center of a sphere (labeled point A in Fig. 1), the radius of which is known as the interaction radius (r_i). The interaction radius (for each polymer material) is used as a fourth parameter in the Hansen method and is empirically determined (using a trial and error approach) as the

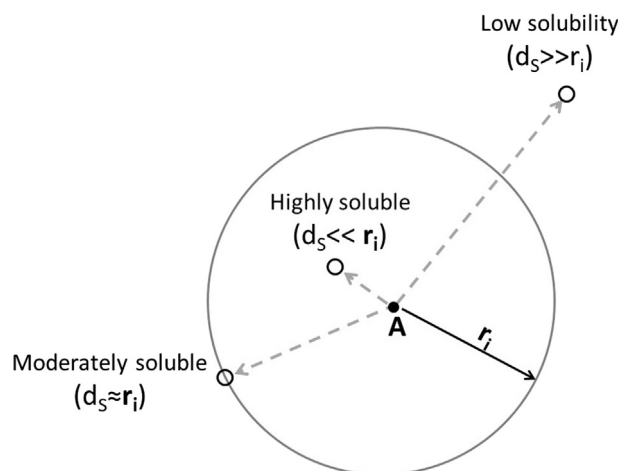


Fig. 2. Two-dimensional representation of Hansen solubility sphere.

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