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Material compatibility evaluation for elastomers, plastics, and metals exposed to ethanol and butanol blends



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HIGHLIGHTS

- Materials were exposed to ethanol and butanol fuels, and aggressive blends.
- Materials examined included elastomers, plastics, and metals.
- Volume and mass changes were measured plus some tensile strength.
- Significant changes in the materials observed for the elastomers.
- Smaller changes were seen for the plastics and the metals.

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ABSTRACT

As the use of alternative fuels increases in the marketplace, it is important to understand how these new fuels might impact the network of transportation, storage, and distribution systems used for transportation fuels. This study examined materials compatibility issues for components that would be found in the existing petroleum fueling infrastructure. E10 blends with both aggressive and non-aggressive formulations, a 55% butanol blend with an aggressive formulation were employed on metal, plastic, and elastomer samples. The material specimens were evaluated before and after exposure for volume and mass change, and elastomers and plastics were tested for tensile strength. The elastomers and plastics generally increased in volume and mass immediately following the exposures, indicating the adsorption of the liquid fuels into the elastomer and plastic material. Following drying, the most elastomers shrank to volume/mass values below that of the original sample, indicating that the liquid fuel and some of the associated elastomer components were removed from the sample, while plastics retained some of this volume swell/mass gain after drying, indicating that the liquid fuel was retained in the plastic structure. Metal samples were the least affected by the liquid fuel exposures, with all samples showing a minimal increase or decrease in volume of 6% or less and negligible change in mass. Most elastomers and plastics showed a reduction in tensile strength and elongation after the fuel exposures.

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1. Introduction

An extensive and pervasive network of transportation, storage, and distribution systems evolved for transportation fuel over many decades around reliability criteria associated with petroleum-based fuels. These pipelines, tank farms, etc., constitute legacy systems that cannot and will not reasonably, quickly, or easily be

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replaced or superseded. There is a transition to greater use of alternative fuels, however, that may come from many different sources, and can be produced through diverse pathways and technologies and in disparate formulations. Of further concern, the new generation of alternative fuels will likely be deployed initially as blends with conventional fuels. Conventional fuels, moreover, are already blended with ethanol and biodiesel fuel. These new fuels could blend seamlessly with current ones, or the new blends could present unanticipated synergistic effects. The American Society of Testing and Materials (ASTM) standards, for example, ensure these new alternative fuels' proper interaction with existing engines, but

do not directly address subtle potential infrastructure issues. The infrastructure must be able to accommodate as many of these new fuels as possible, to allow the greatest flexibility in adoption and utilization of petroleum alternatives.

For liquid fuels, the Energy Independence and Security Act (EISA) of 2007 and the Renewable Fuel Standard (RFS) have been key drivers for the expansion of renewable fuels, requiring the volume of renewable fuels used in transportation to increase to 36 billion gallons per year by 2022. Ethanol is the most widely used renewable fuel, however, there are concerns about the potential for ethanol to adversely impact the compatibility of materials and components used in the existing petroleum infrastructure. Ethanol is obtained from biomass sources including corn, sugar cane, sugar beet, sorghum, grain, switch grass, kenaf, cassava, molasses, wheat, and other biomass, as well as many types of cellulose wastes and harvests [1]. In the U.S., ethanol is currently blended into gasoline at a concentration of 10% by volume (E10). The addition of ethanol to gasoline presents some challenges, since ethanol has rather different physical and chemical characteristics than gasoline, which could potentially affect the performance and efficiency of spark-ignition (SI) engines. Because key volatility properties are changed when ethanol is used, the final gasoline/ethanol blend needs to be formulated to ensure that its properties are within the specifications for the appropriate geographical region and season. Ethanol is highly water soluble, making it potentially incompatible with the existing infrastructure and pipeline transportation processes due to the risk of water-induced phase separation [2].

Butanol is another higher-chain alcohol that shows promise as an alternative fuel for use in SI engines [3]. Butanol is a four carbon alcohol compound, which exists as four different chemical isomers depending on the location of hydroxyl group (–OH) and the carbon bond structure. Butanol offers a number of advantages over ethanol for transportation use. Butanol is less corrosive than ethanol, has a higher energy content than ethanol, and more closely resembles gasoline [4]. In comparison to ethanol, butanol is less susceptible to water contamination, potentially allowing its use in existing distribution pipelines, whereas ethanol must be transported via rail or truck. Butanol has a lower volatility than ethanol and thus less tendency toward cavitation and vapor lock problems [5,6]. Analogous to ethanol, butanol can be produced from either thermochemical pathways (such as synthesis gas to mixed alcohols) or biochemical pathways (such as fermentation). Historically, butanol has been produced by *Clostridia* via acetone–butanol–ethanol (ABE) fermentation processes. Recently, the use of genetically enhanced bacteria has increased the productivity of fermentation process. It is expected that sustainable and cost effective process for butanol production will be realized in the near future [7,8].

Currently, there is very limited information available in the open literature about the potential impacts of alcohol fuels on storage and infrastructure materials. Most of the research in this area has been conducted by Kass et al. [9] at Oak Ridge National Laboratory (ORNL), where they performed a series of studies to evaluate the potential impact of different alcohol blends on fuel storage and fuel dispensing infrastructure materials. The first phase of this research focused on intermediate ethanol levels (10–25%) and evaluated the impacts on elastomers, metals and sealants [9,10]. This effort was then expanded to include plastics, which are found in fueling infrastructure systems, including piping and underground storage tanks [11]. More recently, Kass and coworkers have expanded their research to include butanol blends [12–14]. The same group of authors has conducted studies of the compatibility of off-highway diesel fuel and a 20% pyrolysis bio-oil blend with infrastructure plastics and elastomers [15]. Other studies were conducted by researchers Minnesota State University (MSU). These tests were conducted in response to a 2005 legislature bill in

Minnesota requiring the average gasoline content in the State to contain 20% ethanol by sometime between 2010 and 2013. The tests included similar material compatibility studies of elastomers, plastics, and metals for E10 and E20 blends [16–18]. Note that these studies were all conducted with aggressive ethanol and butanol blends, designed to provide potentially greater impacts over the durations of the test exposures, which are relatively short in comparison with the long terms exposures in real-world applications.

The goal of this work is to further evaluate the compatibility of infrastructure materials with ethanol and butanol blends, with an emphasis on a non-aggressive ethanol blend and a higher butanol blend. For this study, 10% ethanol (E10) blends with both aggressive and non-aggressive formulations, and a 55% butanol blend with an aggressive formulation were tested. Metal, plastic, and elastomer samples used in the infrastructure for the transport and distribution of petroleum products were exposed to these fuels for varying periods of time. These exposures were done in a cylindrical stir chamber for the liquid fuels. The material specimens were evaluated before and after exposure for mass loss, volume change. Elastomers and plastics were also tested for tensile strength after drying.

2. Experimental method

2.1. Test fuels

A total of three liquid fuels were employed in this study. This included an E10 aggressive formulation (CE10A), a 55% butanol with aggressive formulations (CB55A), and a 10% ethanol blend without an aggressive formulation (E10). The CE10A was selected to provide a baseline comparison point to previous studies, while the E10 blend was selected to better understand how the results would be impacted if the aggressive formulation was not used, as this has not been evaluated in previous studies [12–14]. The CB55A blend was selected because it is about the highest level of butanol that can realistically be blended into gasoline while maintaining an acceptable drivability index, and it represents a much higher blend of butanol than has been used in previous studies. For the two aggressive blends, aggressive ethanol and butanol were blended with a reference fuel C. Reference fuel C is a mixture of 50% isooctane and 50% toluene. The aggressive ethanol and butanol fuels contain contaminants that potentially could be found in the liquid fuel infrastructure system at varying levels. Aggressive ethanol contains 99% ethanol, 1% water, 5 ppm sodium chloride, 25 ppm sulfuric acid, and 75 ppm acetic acid [19]. The base ethanol for this fuel was a standard fuel grade ethanol. The aggressive ethanol composition was used as the basis for the construction of an analogous aggressive isobutanol formulation [12–14]. The aggressive butanol formulation contained 99% butanol, 1% water, 5 ppm sodium chloride, 25 ppm sulfuric acid, but with 109 ppm of isobutyric acid instead of the 75 ppm acetic acid. E10 was a fuel blended to represent a typical California gasoline that contained 9.96% ethanol, 21.8% aromatics, and 5.1% olefins, had a specific gravity of 0.7474, and a heat of combustion of 41,998 kJ/kg.

2.2. Material samples

The test materials for the main test program consisted of metals, plastics, and elastomers. A listing of test materials is provided in Table 1.

2.2.1. Metals and alloys

The metal specimens include both bare metal and plated samples. The metals selected are ones that are commonly found in the fueling infrastructure. Steel is used in underground storage

Table 1
List of the material samples.

| Elastomers | Plastics | Metals and alloys |
|--------------------------------|---|---|
| Viton A401C (A401C) | Thermoplastics | Bare metals |
| Viton B601 (B601) | Polyphenylene Sulfide (PPS) | 304 Stainless Steel (SS304) |
| Styrene Butadiene Rubber (SBR) | Polyvinylidene Fluoride (PVDF) | 316 Stainless Steel (SS316) |
| Nitrile Butadiene Rubber (NBR) | Polytetrafluoroethylene (PTFE) | 1100 Aluminum (AL1100) |
| Natural Rubber (NR) | Polyethylene Terephthalate (PET) | 2024 Aluminum (AL2024) |
| Polyurethane (PU) | High Density Polyethylene (HDPE) | 6061 Aluminum (AL6061) |
| Neoprene (N) | Different Nylon Grades (6, 6/6) | Nickel 200 (N200) |
| Buna-N Cork Blend (BN) | Polybutylene Terephthalate (PBT) | Cartridge Brass (CB) |
| | Polypropylene (PL) | Phosphor Bronze (PB) |
| | Polyoxymethylene Acetal Copolymer (POMAC) | 4140 Steel (S4140) |
| | PET Co-polymers (PETG and PETP) | Zinc |
| | Polyvinyl Chloride (PVC) | Fully plated specimens |
| | | Galvanized (zinc-plated) Steel (GS) |
| | | Chromium-plated Brass (CPB) |
| | | Chromium-plated Steel (CPS) |
| | | Nickel-plated Aluminum (NPA) |
| | | Nickel-plated Steel (NPS) |
| | | Electroless Nickel-plated Aluminum (ENPA) |

tanks and piping systems. Aluminum is used in turbine pumps, valves, and nozzles. Other materials, such as bronze, brass, and nickel are used in connection, valves, swivels, and other applications. The plated samples were tested with full plating.

2.2.2. Elastomers

Elastomers are important components of dispenser systems and are used in sealing applications.

2.2.3. Plastics

Plastic materials are also widely used in fuel storage and fuel dispensing applications. Plastic materials are divided into two categories: thermoplastics and thermosets. Thermoplastics were the focus of this study. Thermoplastics are pliable and do not change their chemical composition when heated. Applications for thermoplastics include flexible piping systems, including as permeation barriers and liners, or as reinforcement and support for the flexible piping.

2.3. Sample preparation

Samples were cut from larger sheets into the size needed to fit the mounting fixture. Samples were all cut to similar dimensions. The sizes for the samples ranged from 2.145 to 2.86 in. (5.45–7.26 cm) in length, 0.7325 to 0.9315 (1.86–2.37 cm) in width, and 0.112 to 0.2745 (0.28–0.70 cm) in thickness. The total sample surface area for the samples ranged from approximately 24.4–47.9 cm², with an average surface area of 36.2 cm². Plastic and metal samples were cleaned with an ultrasonic bath in a solution of simple green soap and water. Metal samples had an additional acetone wash.

The mounting fixtures for the samples are designed to hold samples in place and isolate them from each other using Teflon spacers and washers. A Teflon crevice washer was placed between each sample to prevent sample-to-sample contact. A nut and bolt assembly was used to hold the samples onto the bracket.

2.4. Stir chamber preparation

A stir chamber was used to evaluate the impact of different fuels on metals, plastics, and elastomers used in the infrastructure for the transport and distribution of petroleum products. The stir chamber is described briefly here and in greater detail in Durbin et al. [20]. The stir chamber was designed to allow exposure of different types of materials to different types of fuels over a period of several weeks/months.

The stir chamber was a stainless steel chamber 17" high with a circumference of 14" that housed mounting brackets for different samples. The stir chamber had a paddle that was rotated at a constant speed to maintain a flow in the chamber. The chamber was heated to a temperature of 60 °C for these experiments. Heater coils were placed on the outside of the stainless steel drum to enable the heating of the drum to the 60 °C required for the testing. The heating system had a power rating of 1200 W and is controlled by a Love Controls series No. 2600 heater controller. The temperature inside of the stir chamber was measured by a thermocouple that is connected through the top of the chamber.

A total of 4 of each type of plastic and elastomer samples and 3 of each type of metal samples were used in the stir chamber for each fuel exposure. For the plastic and elastomer sample types, 3 samples of each type were immersed in the fuel. For the metal sample types, 2 samples of each type were immersed in the fuel. The other samples were placed above the liquid line to provide exposure to the fuel vapors. The results for the fuel vapor exposed samples are provided in Durbin et al. [20].

A total of 6 stir chambers were used. For each fuel, the plastics and elastomers were exposed in one chamber while the metals were exposed in another. The stir chamber exposures were conducted for a period of 4 weeks for the metal and elastomer samples and 16 weeks for plastics. The stir chamber was sealed for the duration of the test, with the exception of when it was opened to remove the elastomer samples from the chambers that also included plastics. The same fuel was used for the duration of the exposures without changing it out.

2.5. Materials testing

The metal, elastomer, and plastic testing included measuring volume and mass change, on each specimen exposed in liquid phases of test fluids. The tests included measuring both wetted and dried specimens. Measurements of tensile strength were also made for elastomer and plastic tests.

Prior to and subsequent to the fuel exposures, the weights and dimension of the samples were measured and recorded. The sample weights were measured with a Mettler Toledo AE100 balance, capability of measuring to 0.0001 g, and the sample dimensions/volumes were measured with a micrometer. For the post-exposure analyses, the samples were weighted and measured for volume change in a wet state (i.e., immediately after removal from the stir chamber prior to drying) and in a dry state. For the dry state, the samples were dried at 60 °C for 20 h for the elastomer

samples and for 65 h for the plastic samples. Samples were also evaluated for any changes in visual appearance before and after exposures, as described in Durbin et al. [20].

Tensile strength properties were measured using an Instron 5969 model tensile strength tester, with a 50 kN load cell. These properties included tensile strength as well as tensile elongation. Tensile strength was calculated by the maximum load in pounds-force at the time of failure divided by the average cross-sectional area of the material in square inches. The percent elongation was determined by measuring the change in gage length from the original specimen to the fuel affected specimen. The tensile strength test was conducted on one sample that is not placed in the stir chamber for each of the plastic and elastomer samples, and on one plastic and elastomer sample immersed in the liquid fuels. Samples were machined to the correct dimensions to fit in the tensile strength tester following drying and their final weighing, mass determination, and characterization of their visual appearance.

3. Results and discussion

The material exposure results are presented in the following section. This includes the results in terms of volume change, and mass change for elastomers, plastics, and metals. Tensile strength results are also included for elastomers and plastics.

3.1. Volume change

3.1.1. Elastomers

The majority of the elastomer samples increased in volume when wet and then decreased in volume when dried. Elastomers generally showed greater volume changes compared to the plastics or metals. Comparisons between wet and dried samples that were exposed to the fuel directly can be seen in Fig. 1a and b, respectively, for the before and after drying exposures. NR and NBR samples are missing information for the CE10A exposure due to damage, while B601 was not available for the E10 exposure.

Before drying, CE10A and CB55A fuels caused SBR to have the largest change at about 156% and 41% for submerged samples, E10 caused an average change for SBR at 19%. Fluorocarbons (A401C, B601) generally showed the smallest volume change after exposure to the different fuels, with less than a 16% volume increase. NR and NBR were only available for the E10 and CB55A fuels, which had an average percent volume change of about 92–95% and 31–43%, respectively. N showed volume changes from a 61% increase to a slight decrease in volume for the liquid exposures, with again the CE10A showing the greatest increases and the E10 showing the smallest volume changes. PU showed volume increases ranging from 15% to 37% for the liquid exposures for the CE10A and CB55A exposures, respectively. The E10 fuel showed volume changes of less than 5% for PU. The BN samples also show a wider range in volume change from –17% to 41% for the liquid exposures, with CB55A showing the greatest increases and E10 showing the smallest volume decreases.

After drying the SBR samples shrank to 90–96% of their original volume. NBR showed decreases of 17% below the original sample volume for the CB55A exposures and of 12% below the original sample volume for E10 exposures. The B601 retained about a 10% increase in volume for E10, while the A401C showed mixed results some samples showing volume reductions and others showing volume increases compared to their original volume. BN lost about 15–23% of their original volume, while PU retained close to 5% of the increased volume for the CB55A, but decreased up to 6% below its original weight for the E10 exposures.

These results are generally consistent with the results from previous studies. Kass et al. [9–13] found some of the largest gains for SBR, followed by NBR and N (60–80% increases for lower level ethanol/butanol exposures), and PU (approximately 40% for the different aggressive alcohol blends), with the fluorocarbons swelling from 15% to 22% for A401C and B601 for alcohol fuel exposures. They also found trends where the volume swell tailed off as a function of increasing ethanol/alcohol level for several

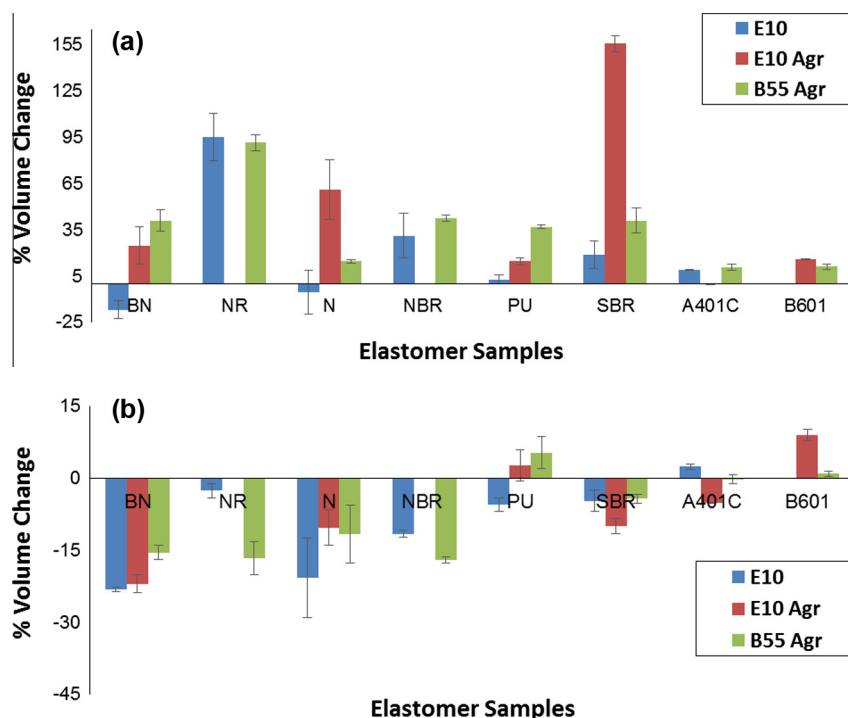


Fig. 1. Percent volume change of elastomer samples before drying (a) and percent volume change of elastomer samples after drying (b). Errors bars represent ± one standard deviation.

materials, including SBR, NBR, and N, with a slight trend for the fluorocarbons. After drying, they found volume reductions on the order of 15–18% for SBR, 10–18% for NBR, 17–20% for N, from 1% to 12% for PU, and a more consistent retention of about 7% for the fluorocarbons [9–13]. Jones et al. [16] evaluated elastomers for volume changes for CE10A and CE20A fuels, including nitrile rubber with a medium and high CAN content and fluoroelastomers. For fluoroelastomers, they found somewhat higher volume increases before drying from 33% to 41%, and increases of 8% to 12% after drying for CE10A and CE20A. For the NBR samples for the CE10A and CE20A exposures, they found increases of 69–70% for the medium CAN content samples and 26–28% for the high CAN content samples, and reductions of 6–19% after drying.

The volume expansion of a given fuel upon fuel exposure can be understood in terms of the mutual solubility between the material and the fluid or fuel. Solvents (test fuels) and solutes (elastomers) having similar solubility parameters will have a greater affinity for permeation and dissolution than those with dissimilar values. Kass and coworkers have performed a series of solubility potential calculations using the Flory–Huggins model with the Hansen solubility parameter methodology [11–14]. Using this methodology the relative volume swell can be assessed by comparing the solubility distance for each material to the interaction radius of the polymer. If the solubility distance falls within the interaction radius, then moderate to high solubility can be expected. If the solubility distance is equal or similar to the interaction radius, then low to moderate solubility is expected. If the solubility distance is greater than the interaction radius, then negligible to low solubility is expected. For the elastomer materials evaluated by Kass et al. via this analysis, moderate to high swelling was predicted for SBR, NBR, and N, whereas low to moderate swelling was predicted for fluoroelastomers and PU. This is consistent with the results found in our study. The solubility analysis also predicted higher swelling for elastomers for fuels containing alcohols, with ethanol based fuels showing a greater potential for swelling compared to butanol.

The volume reductions after drying represent a different phenomena, where the test fuel is being removed from the elastomer.

For samples shrinking to volumes less than their original sample volume, this indicates the dissolution and extraction of one or more of the components for the elastomer in addition to the removal of the fuel. For elastomers, these components could be plasticizers that are typically phthalate chemicals added to improve pliability. The removal of these plasticizers could lead to embrittlement or the potential to crack under compression.

3.1.2. Plastics

Fig. 2a and b presents the comparison of percent volume change of wet and dried plastic samples, respectively, that were exposed to E10, CE10A, and CB55A fuels, with error bars representing one standard deviation. The majority of the plastic samples increased in volume after exposure. The samples had the largest volumes immediately after removal from the chamber, while wet. After drying the samples shrank, but still had a larger volume then their original measurements, as seen in Fig. 2a and b.

Before drying, the plastic generally showed smaller volume changes than the elastomers. N6, N6/6, PBT, PET, PETP, PPS, PVDF, POMAC, and PTFE increased less than 10% for all samples. PVC and PETG showed the strongest effects for the plastic samples. PVC samples were strongly affected by all fuels with an expansion of 27–34% for all samples, with CE10A showing the largest increases. PETG increased the most for CB55A at 31%. E10 caused a notable volume change of 16% for HDPE and PL. CE10A and CB55A caused smaller changes to HDPE at less than a 10% increase when wet.

After drying, the majority of the plastic samples had an increase in volume of 5% or less from their original dimensions. PVC and PETG retained a majority of the increased volume at 19–29%. PL shrank in volume more than HDPE after drying. PL retained less than 5% of the volume increase, while HDPE retained anywhere from 5% to 8% of the volume increase after drying. These results are generally consistent with the results from previous studies. Kass et al. [11,12,14] found increases of less than 5% for PPS, PET, PTFE, POMAC, and PBT, with greater volume increases for PETG (~25% for the lower level aggressive alcohol blends), and increases of approximately 10% for HDPE. After drying, they found samples

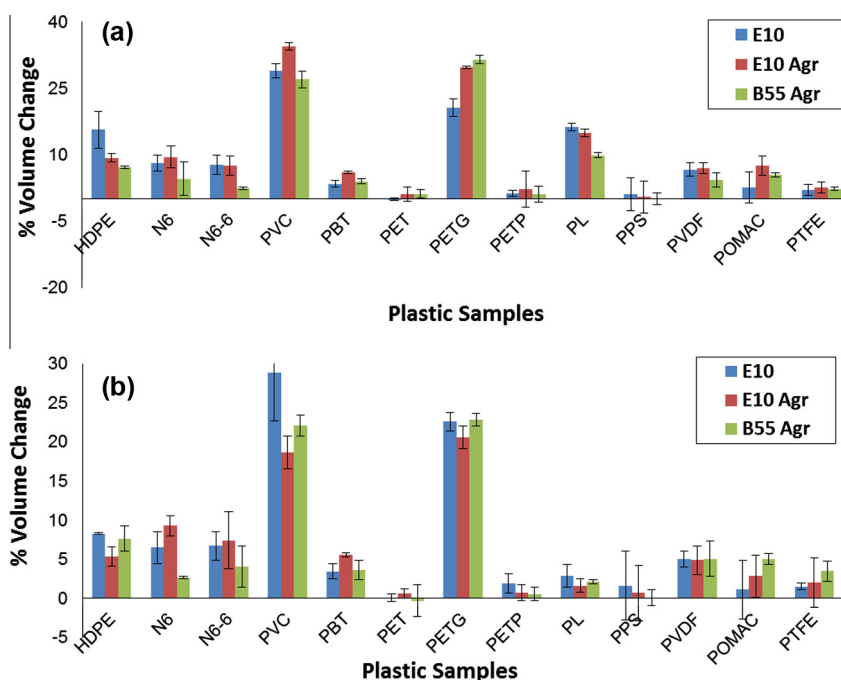


Fig. 2. Percent volume change of plastic samples before drying (a) and percent volume change of plastic samples after drying (b). Errors bars represent \pm one standard deviation.

retained some of their volume swell, with increases of 5% or less for PPS, PET, PTFE, POMAC, PBT, and PVDF, an increase of 2% or less most N6 and N6/6 exposures (somewhat lower than ours), increases of approximately 8–15% for PETG, and similar dry volume changes to ours for HDPE. Jones et al. [17] studies showed volume increases of 10% or less for most materials exposed to CE10A and CE20A fuel blends, including N6, N-66, PBT, PET, and polyetherimide 1010 moldable (PEI). The findings of this study showed the largest volume increases of 55–60% for polyurethane 55D-90 Adurameter hardness (PUR) for the E10 and E20 blends, which was not tested in our study. The authors did, however, show about a 35% reduction in volume for PVC, which was not seen in either our study or the Kass et al. [11,12,14] studies.

The results can also be evaluated against solubility analysis calculations. For the plastics, these calculations indicated that the plastics most susceptible to volume swell would be PTFE, PTEG, and PP [11–14]. The higher volume swell was observed for PTEG, but not for PTFE. The solubility analysis also showed relatively low levels of solubility for PVDP, while the experimental results showed higher levels of volume swell than expected. The solubility analysis also predicted higher swelling for plastics for fuels containing alcohols, with ethanol based fuels showing a greater potential for swelling compared to butanol.

3.1.3. Metals

Fig. 3a and b shows the percent volume change of wet and dried metal samples, respectively, that were exposed directly to E10, CE10A, and CB55A fuels, with error bars representing one standard deviation. Wet and dried metal samples showed relatively minor volume changes, and in many cases the error bars were larger than the measured change, indicating that the changes were within

the variability of the measurement. The CB55A exposures showed a tendency to increase metal sample volumes after drying. On the other hand, the majority of metal samples exposed to CE10A decreased in volume slightly after drying. The E10 results were more mixed. The metal samples all had a minimal increase or decrease in volume of 6% or less. The relatively minor volume changes after the fuel exposures is consistent with the results from other studies [9–12,18].

3.2. Mass change

3.2.1. Elastomers

Fig. 4a and b shows the average percent weight change of the elastomer samples exposed to E10, CE10A, and CB55A before and after drying, with error bars representing one standard deviation of the measurements. BN, N, NR, NBR and SBR samples that were exposed to E10 and CB55A are missing data for the liquid exposures due to evaporation and stabilization issues while weighing. However, big changes were observed for BN, N, and SBR samples for other fuel exposures. Elastomers increased in weight while wet and generally decreased to below their original weight when dried. Also, the samples for the CE10A exposures showed generally the most remaining mass, whether the sample increased or decreased in mass. Elastomers generally had the greatest change in mass of all the material types for both wet and dried conditions, which can be seen in Fig. 4a and b.

Before drying, all of the samples increased in weight. BN, N, and SBR had the largest weight changes of all of the samples, even though many samples could not be measured accurately on the scale, due to evaporation during the weighing process or excessive damage. The percent weight change of SBR increased the most, more than doubling for exposure to CE10A. BN and N increased 46–61% after exposures to CE10A. PU showed an

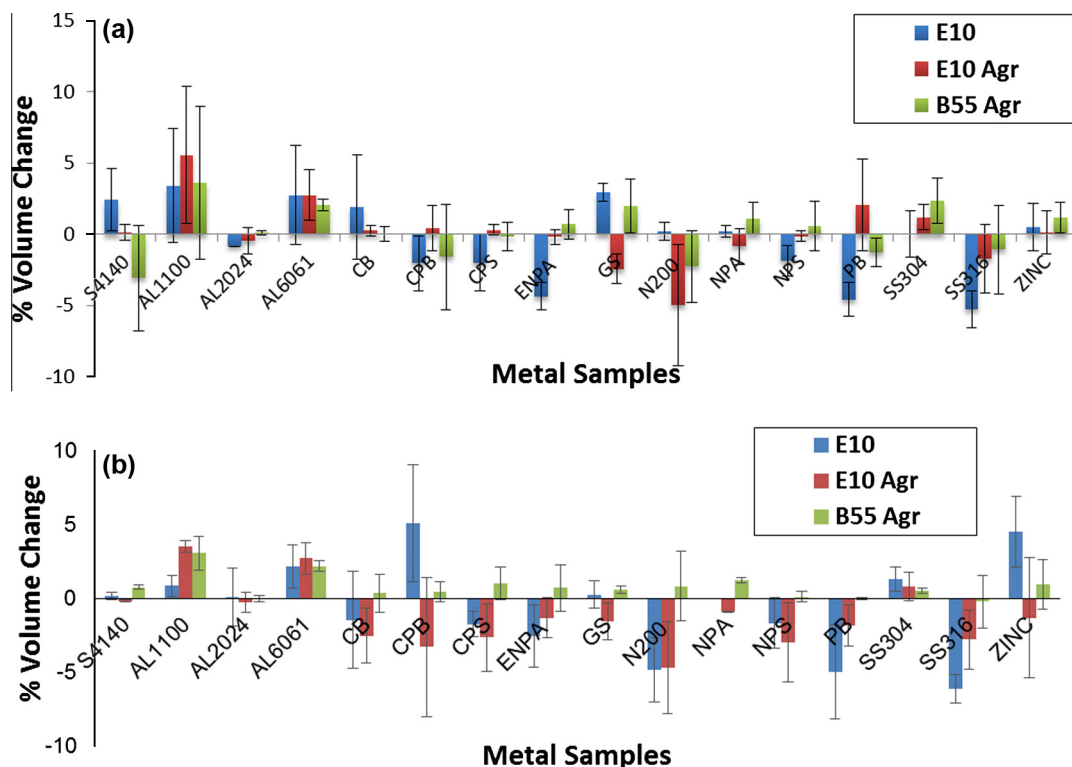


Fig. 3. Percent volume change of metal samples before drying (a) and percent volume change of metal samples after drying (b). Errors bars represent \pm one standard deviation.

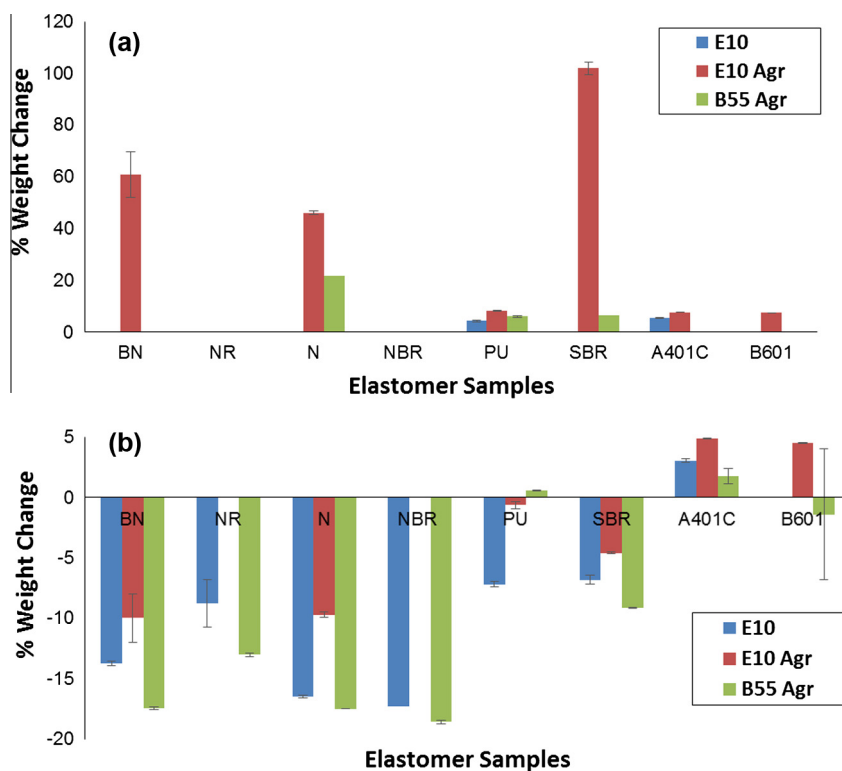


Fig. 4. Percent weight change of elastomer samples before drying (a) and percent weight change of elastomer samples after drying (b). Errors bars represent \pm one standard deviation.

increase of 8% or less for all fuels. Overall, the fluorocarbons showed the smallest increases of less than 8% for the submerged samples.

After drying, the elastomers all decreased below their original weights mostly in the range of 5–20%, except the fluorocarbons (A401C and B601), which maintained about a 5% increase in weight. The BN, NR, N, and NBR samples all exhibited weights between 9% and 19% below their original weights, with the CE10A samples generally showing the smallest weight loss and the CB55A samples showing the largest weight loss. SBR had a percent weight change of roughly 5–10% below its original weight after drying. The PU samples after drying had weights comparable to their original values prior to exposures for CE10A and CB55A, and showed decreases of 7% for E10 exposures.

The mass increases after fuel exposures were comparable to those found by Kass and coworkers. They found larger increases for SBR (65–75%) and N (40–50%), and smaller increases for PU (20–30%) and the fluorocarbons of 6–10% [9,10,12,14]. After drying, they also found mass decreases of for most elastomers, including 8–13% for NBR, about 14% for N, about 10% for SBR, and a mass decrease of 6–13% for PU for alcohol fuels, with a slight retention of mass for the fluorocarbons (A401C and B601) [9,10,12]. In the Jones et al. [17] study, for fluoroelastomers, they found similarly low mass increases before drying of around 12%, and increases of 4–5% after drying for CE10A and CE20A. For the NBR samples for the CE10A and CE20A exposures, they found mass increases of 28–29% for the medium ACN content samples and around 10% for the high ACN content samples, and reductions of 7–10% after drying.

3.2.2. Plastics

Plastics did not have major changes in weight compared to the elastomers. Fig. 5a and b shows the weight percent change of plastic samples exposed to E10, CE10A, and CB55A before and after

drying, with error bars representing one standard deviation. The different types of plastics tested either maintained most of their original weight or increased in weight after exposure to the various fuels. The samples generally remained heavier than their original weight after being dried, depending on the type of plastic. In general, the samples had a similar change in weight as they were exposed to the liquid fuels.

Before drying, the majority of the plastic samples besides PVC, PETG, and PL had a weight increase of 10% or less, with the majority of wet samples showing an average increase of less than 5% in weight. PVC and PETG had the greatest percent increase in weight at 13–22%. PL had a smaller average weight change of 9%, when exposed to CB55A for wet samples. Nylon samples (N6, N6/6) had weight increases of 6% or less. The Nylon samples were most affected by CE10A, but showed minimal impacts for exposure to CB55A. The HPDE samples showed increases of 8% or less for the fuel exposures. CE10A generally had the greatest effect on weight change for plastic samples. The most resilient plastics are PBT, PET, PETP, PPS, PVDF, POMAC and PTFE, which had a change of less than 4% from their original weight for all samples exposed to E10, CE10A, and CB55A, as seen comparing Fig. 5a and b.

After drying, all plastic samples except for PVC and PETG had an increase of less than 5%, with the majority of the dried samples having a weight increase of 2% or less. PVC and PETG retained some of the weight at an 8–11% increase compared to their original weight. Nylon samples (N6, N6/6) had a weight increase of 5% or less. PL lost most of the increased weight and shrunk back down to near its original weight. The HPDE samples showed increases of 2% or less after drying, with E10 showing slightly higher weight changes compared to the other fuels.

The results are similar to those from previous investigations [12,14]. Kass and colleagues found mass increases of 15% before and 10% after drying for PVC and PETG, of 7% before and 1% after drying for HDPE, and of 6–7% before and 2–3% after drying for

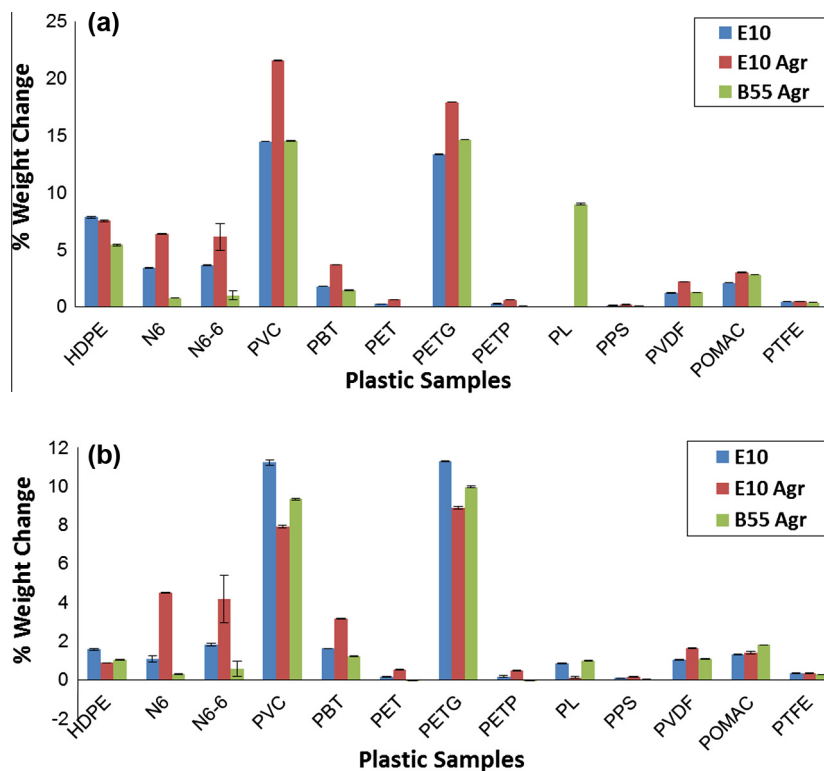


Fig. 5. Percent weight change of plastic samples before drying (a) and percent weight change of plastic samples after drying (b). Errors bars represent \pm one standard deviation.

nylon for E25 but less than 1% for other fuels. They also showed similarly for most of PBT, PET, PETP, PPS, PVDF, POMAC and PTFE materials that mass increases were small for both the wet and dry mass [12,14]. Other studies dealing with CE10A and CE20A blends showed mass increases of between 3% and 10% for N6, N-66, PBT, and PET, mass reductions of 31–33 for PVC, and large mass increases of 41–52% for PUR [17]. Again the mass reductions for Jones et al. were in contrast to the results seen in the Kass et al. [12,14] studies and in our study.

3.2.3. Metals

Metal samples that were exposed to E10, CE10A, and CB55A showed a negligible change in weight for samples exposed to the fuels. Fig. 6a and b shows the percent weight change for all of the metal samples exposed to E10, CE10A, and CB55A that were wet and dried, respectively, with error bars representing one standard deviation. Submerged samples did not deviate past 1/10 of a percent in weight change after fuel exposure and drying. The relatively minor mass changes after the fuel exposures is consistent with the results from previous works [9–12,18].

3.3. Tensile strength

The tensile strength of a material is the maximum stress it can withstand while being pulled or stretched before it breaks or fails. Tensile strength was calculated by the maximum load in pounds-force at the time of failure divided by the average cross-sectional area of the material in square inches. The percent elongation is another property measured with the tensile strength test. The percent elongation was determined by measuring the change in gauge length from the original specimen to the fuel affected specimen.

3.3.1. Elastomers

Fig. 7a and b represents the percent change of tensile strength for exposed elastomer samples exposed to E10, CE10A, and CB55A. PU, NR, NBR, and BN showed the biggest reductions in tensile strength. PU showed reductions from 43% to 92%, with the CB55A samples showing the smallest change. NR showed reductions from 84% to 92% in tensile strength for the liquid exposures. NBR showed reductions from 43% to 49%. The BN shows reductions from 43% to 62%, with CE10A showing the largest reductions. The Viton A sample for CB55A and the Viton B sample for CE10A exposures also showed reductions of 28% and 36%, respectively. The other materials showed changes of 25% or less. Most samples became less resistant to stress after fuel exposure, but SBR and N showed an increase in tensile strength when exposed to the E10 fuel.

The percent change in elongation is shown in Fig. 7a and b for the elastomer samples. The NBR and NR samples lost approximately 90% and 62–80%, respectively, of their elongation. The large reduction in the elongation for the NBR samples is consistent with the visual results that showed the samples breaking apart after exposure and then showing embrittlement when they were dried. The PU samples showed reductions in elongation of 82% for the E10 fuel, but smaller reductions in elongation for the two aggressive fuel blends. SBR showed reductions in elongation ranging from 9% to 53%, with the smallest reductions for the CE10A fuel and the largest reduction for CB55A. The Viton A sample showed less than a 20% reduction in elongation for the other fuel exposures. The other materials showed reductions of approximately 35% or less, with the exception of the N samples exposure to E10, which showed increases in elongation on the order of 30%, and the BN samples, which also showed increases for the liquid fuel exposures.

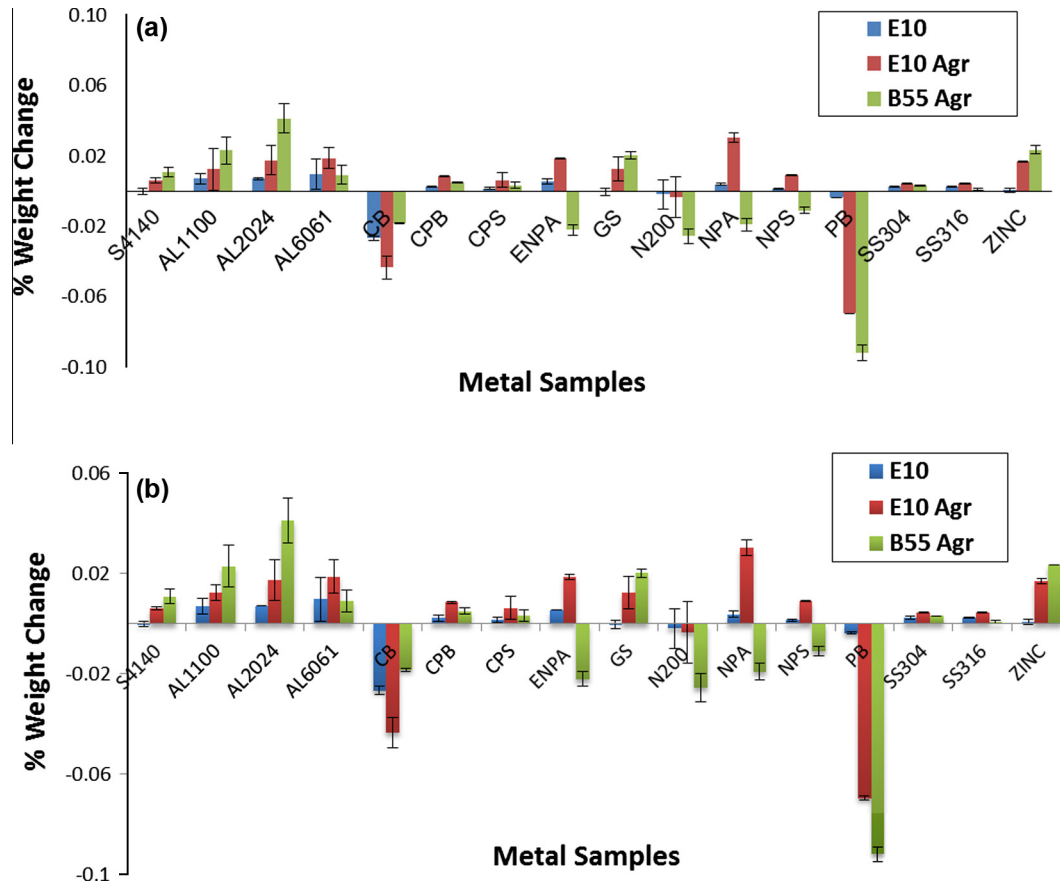


Fig. 6. Percent weight change of metal samples before drying (a) and percent weight change of metal samples after drying (b). Errors bars represent \pm one standard deviation.

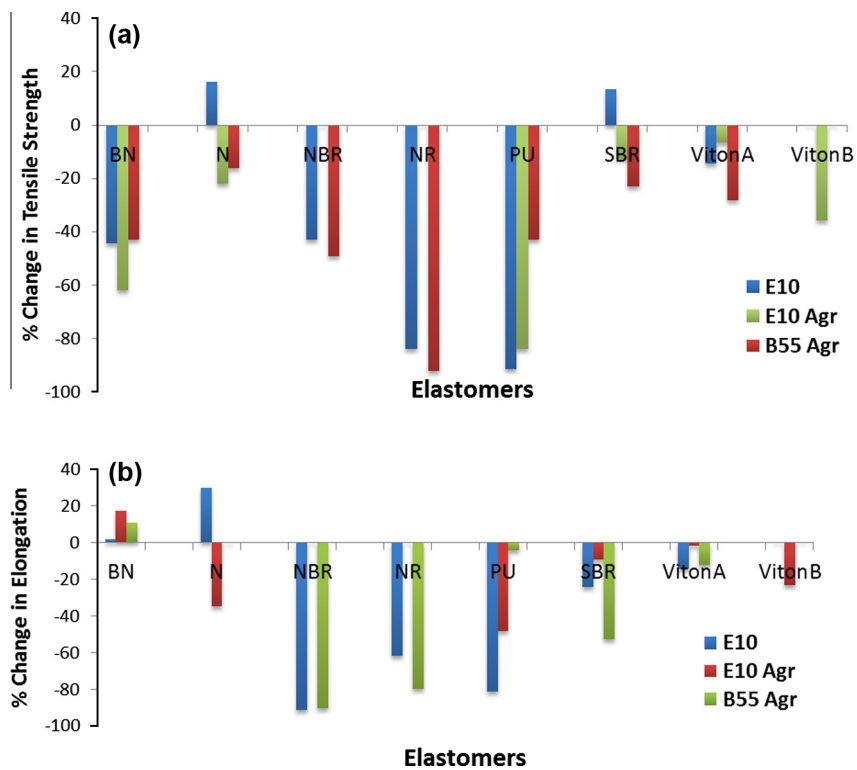


Fig. 7. Percent tensile strength for elastomer samples (a) and elongation change for elastomer samples (b).

Tensile strength tests in a previous study for CE10A and CE20A blends showed tensile strength reductions of between 51% and 53% for fluoroelastomers wet, 9% and 21% for fluoroelastomers dry, 64% and 67% for NBR wet, 11% and a 3% gain for NBR dry [17]. Overall, their results showed somewhat smaller reductions in Tensile strength for the dry samples, which are the most comparable with the methodology utilized in our study. Jones et al. [16] also found very minor changes in elongation (i.e., <1%) for the fluoroelastomers and NBR after drying. Kass et al. [9] also showed reductions in tensile strength for fluoroelastomers and NBR after CE20A exposures.

3.3.2. Plastics

Fig. 8a and b represents the percent change of tensile strength for plastic samples exposed to E10, CE10A, and CB55A. Major changes can be seen in PET exposed to E10, PETG exposed to E10, CE10A, and CB55A, PETP exposed to E10, PL exposed to E10, CE10A, and CB55A, and PVC exposed to E10, CE10A, and CB55A. The majority of these samples weakened by 40% or more, with most fuels for the PETG and PETP showing reductions in tensile strength ranging from 67% to 87%. Notable changes can also be seen in N6 and N6/6 exposed to E10 and CE10A, and PTFE and HDPE exposed to E10, CE10A, and CB55A.

Tensile strength tests in a previous study for CE10A and CE20A blends showed tensile strength reductions of between 26% and 44% for N6, N-66, PBT, PET, and PVC [17]. The results of this study are directionally consistent with and similar in magnitude to the CE10A reported here, with the exception of PET, which showed a relatively small reduction in tensile strength for CE10A. Some of the differences in tensile strength results between the present work and the previous study conducted by Jones et al. [17] could

be that our samples were dried at an elevated temperature before running the tensile test, whereas the samples taken from Jones et al. [17] study were tested within 5 min of being removed from the fluid to prevent drying.

Other samples showed smaller changes in tensile strength, on the order of 10% or less, including N6, N6/6, PET, PBT, and PPS for CB55A exposures, PET, PPS, and PVFE for other fuels. Additionally, HDPE samples showed increases in tensile strength for all three liquids, whereas the other materials showed reductions in tensile strength.

The percent change in elongation is shown in Fig. 8a and b for the plastic samples. The plastics showed reductions in elongation for all samples, but the PVC and some CE10A samples. The PVC showed increases in elongation from 134% to 183%. The majority of the reductions in elongation were on the order of 25–95%. For the samples showing a reduction in elongation, E10 showed the greatest reductions for some materials, but not others. Interestingly, the tensile strength tests from a previous study [17] showed relatively large increases in elongation for some materials for CE10A and CE20A blends, ranging from 162% to 456% for N6, N-66, and PBT, as well as smaller increases for PET and PVC in contrast to the reductions seen here. Overall, it appears that the differences in drying had a stronger impact on the elongation results as opposed to the tensile strength test results.

The results for the tensile strength can also be compared with some previous where other measurements such as hardness and Dynamic Mechanic Analysis (DMA). The hardness test is a measurement of a materials resistance to permanent indentation, while the DMA test measures elasticity and can be used to characterize the glass transition temperature (T_g) or the onset temperature associated with the change from when the molecular

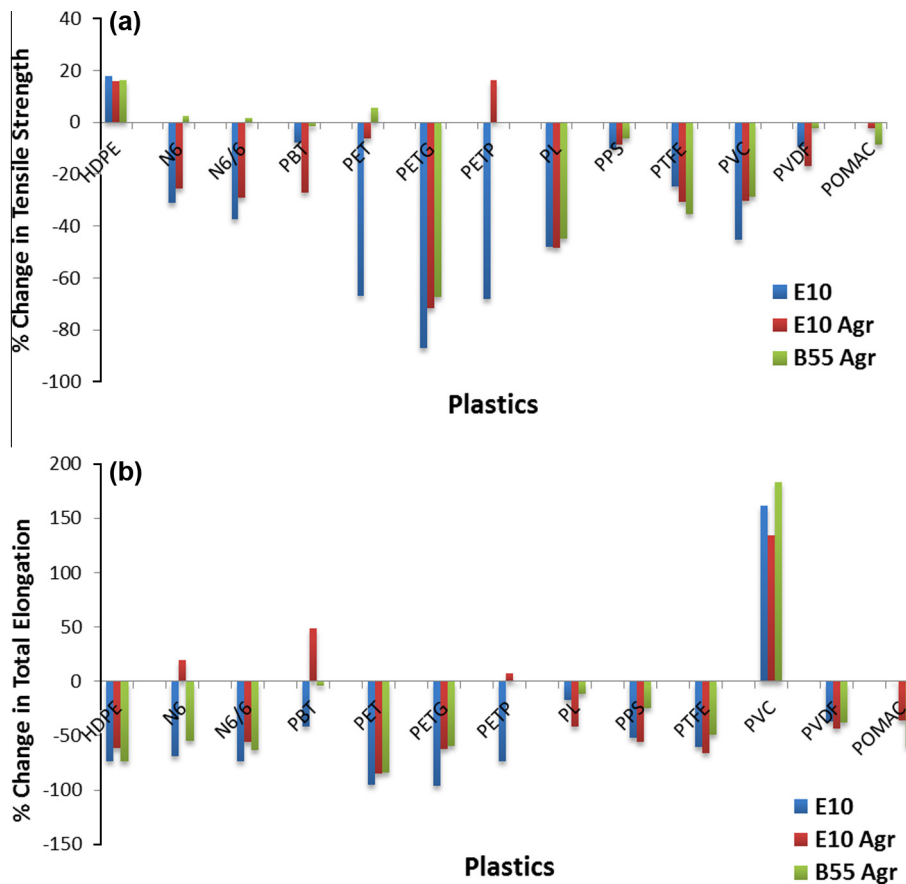


Fig. 8. Percent tensile strength for plastic samples (a) and elongation change for plastic samples (b).

bonding creates a rigid glassy state to when the molecular structure relaxes into a more flexible and pliable state. Elastomers that showed some of the largest reductions in tensile strength and elongation, including NBR, NR, and PU, also showed reductions in hardness in studies by Kass et al. [9–13]. Hardness tests for elastomers in studies by Jones et al. [16] showed reductions in hardness before drying and after drying for fluoroelastomers and before drying for NBR medium and high CAN content samples, but showed increases in hardness for NBR medium and high CAN content samples after drying. The elastomer results for the DMA testing were more mixed, however, with reductions of about 10 °C in T_g for fluorocarbons, which can be attributed to test fuel being retained in the sample that allows molecular relaxation to occur at lower temperatures, increases in T_g on the order of 20 °C for NBR, which suggest the removal of a plasticizer additive that would effectively reduce the operational temperature range of the elastomer, and no significant change in T_g for PU, N, and SBR after fuel exposures [13]. For the plastics, PETG showed relatively larger reductions in hardness, consistent with the relatively large reductions in tensile strength seen in this study, while most of the other plastics showed relatively minor reductions in hardness. PET and PETG also showed larger reductions in T_g , consistent with a larger reductions in tensile strength seen for the PET and PETG, while other plastics, including PPS, PTFE, PDVF, HDPE, and POM, did not show large transitions in T_g [10–12,14].

4. Conclusions

As the use of alternative fuels increases in the marketplace, it is important to understand how these new fuels might impact the network of transportation, storage, and distribution systems that have been developed around reliability criteria associated with petroleum-based fuels. This study examined materials compatibility issues for infrastructure components that would be found in the existing petroleum fueling infrastructure. For this project, E10 blends with both aggressive and non-aggressive formulations, a 55% butanol blend with an aggressive formulation were tested. Metal, plastic, and elastomer samples used in the infrastructure for the transport and distribution of petroleum products were exposed to these fuels for varying periods of time. These exposures were done in a cylindrical stir chamber. The material specimens were evaluated before and after exposure for mass loss and volume change, and elastomers and plastics were tested for tensile strength.

The most significant changes in the materials as a result of the fuel exposures were seen for the elastomers, followed by the plastics, and then the metals. The elastomers and plastics generally increased in volume and mass immediately following the exposures, indicating the adsorption of the liquid fuels into the elastomer material. For the elastomers, the rubber samples (SBR, NBR, and NR) showed some of the largest increases, while the Fluorocarbons (A401C, B601) showed the smallest increase. For the plastics N6, N6/6, PBT, PET, PETP, PPS, PVDF, POMAC, and PTFE increased less than 10% in volume for all samples before drying, while PVC and PETG increased by 21–34% in volume and 13–22% in mass upon exposure. For the metals, all had a minimal increase or decrease in volume at 6% or less, with the CB55A producing increases in volume and the E10 showing decreases for most metals after drying. The metal samples show an insignificant change in mass change, with the majority showing a percent weight change of 0.1% or less. Following drying, the most elastomers shrank to volume/mass below that of the original sample, indicating that the liquid fuel and some of the associated elastomer components were removed from the sample, while the plastics generally retained some of this volume swell/mass gain

after drying, indicating that the liquid fuel was retained in the plastic structure. For the plastics, the majority of samples had an increase in volume of 5% or less from their original dimensions after drying, with the exception of PVC and PETG, which retained between 19% and 29% of the volume increase and between 8% and 11% of the mass gain.

Comparisons can also be made between the different test fuels in terms of weight and volume changes. In evaluating the E10 against the CE10A and CB55A results, the fuels were relatively comparable over the different materials and analyses covered in this study. The CE10A fuel did show some trends of larger volume increases for the wet elastomers, particularly for SBR and N, smaller reductions in weight upon drying for the elastomers, larger weight increases for the wet plastic samples, and slightly larger weight increases for the metals compared to the E10 fuel. The CB55A fuel showed some trends of greater volume increases for the wet elastomers and slightly larger reductions in weight for the elastomers after drying compared to the E10 fuel. Taking the results as whole, however, the CE10A and CB55A fuels appear to impact material compatibility similarly to that of the E10 fuel that was blended without the aggressive components.

Most elastomers and plastics showed a reduction in tensile strength and a tendency for reduced elongation during the tensile strength test. For the elastomers, the biggest reductions in tensile strength were seen for PU (43–92%), NR (84–92%), NBR (43–49%), and BN (43–62%), while SBR and N showed an increase in tensile strength when exposed to the E10 fuel. For the plastics, the largest reductions in tensile strength were seen for PETG and PETP ranging from 67% to 87%, with PET, PL, and PVC also weakening by over 40%, while minimal changes were seen for PPT, PPS, and PVDF and N6, N6/6, and PET. Most elastomers showed changes in elongation of $\pm 50\%$ or less, with a few samples showing larger changes of anywhere from 60% to 90% for various fuel blends, including NBR, NR, and PU. The plastics showed reductions in elongation for all samples, mostly ranging from 25% to 95%, with the exception of PVC, which showed an increase in elongation from 134% to 183%. PET and PETG are the plastics that showed the largest losses in elongation.

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