ASSESSMENT OF COMPATIBILITY OF FUEL SUPPLY SYSTEM POLYMERIC PARTS WITH BIOETHANOL/GASOLINE BLEND E85

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Abstract. Conversion of automobiles to different type of fuel involves evaluation of material compatibility of the new fuel and components of the engine and fuel supply system. Automobiles, equipped with a spark ignition gasoline fueled engine, can be converted to work on gaseous fuels, such as liquefied petrol gas or liquid fuels, such as ethanol/ gasoline blend E85. In case of such conversion, materials in question can be divided in two categories – metallic and polymeric. This study focuses on evaluation of compatibility of the fuel supply system parts made of non-elastomer polymeric and fuel containing up to 85 % of ethanol. Automobile parts which are made of polymeric materials have standardized code markings, required for recycling purposes. The authors propose to use the material code markings to identify the type of polymeric material of the fuel supply system parts. Typical material choice for the main fuel supply system parts is presented and its compatibility with E85 fuel discussed.

Keywords: polymer, plastic, fuel, ethanol.

Introduction

Conversion of automobiles, equipped with a spark ignition engine to run on dual fuel – liquefied petrol gas (LPG) or gasoline, is well known and popular in Latvia. Among other procedures, professional conversion to LPG involves compatibility assessment of certain engine components, such as exhaust valve seats. The conversion of automobiles to other fuel types requires specific groundwork to ensure that the converted automobile is safe and reliable.

There are efforts in many developed countries to reduce the consumption of fossil fuel as an energy source in transportation. Some countries require addition of ethanol to the gasoline sold to consumers. For instance, regular summer type gasoline of brand A95 in Latvia contains 5 % of anhydrous ethanol. E85 is spark ignition engine fuel, which contains approximately 85 % ethanol and 15 % gasoline.

Use of E85 in the automobile, designed for regular gasoline, requires an adaption device to increase the fuel quantity in the engine cycle and improve the engine cold start capabilities. Operational parameters of automobiles running on ethanol-gasoline blends were defined by Aboltins et al. 2010 [1]. Automobiles, designed by producers for E85 use, normally have high compatibility of fuel and fuel supply system materials. If the existing automobile, built for fuelling with regular gasoline, is selected to be converted for E85 use, its fuel system components must be inspected and evaluated for compatibility with the new fuel. The automotive industry was aware of the upcoming requirements for adding oxygenates, such as MTBE, ETBE and ethanol to regular gasoline [2]. Wide scale application of polymeric materials in automotive industry was introduced in 1990s. Parts, which typically were produced form metallic alloys, are now being made from different polymeric and composite materials. The globalization of the automotive industry leads to merging and close cooperation of former competitors and independent producers. The same applies to the manufacturers of the components and materials. Design of fuel supply systems of the current fleet of automobiles relays on typical solutions, particularly on the choice of materials [2]. The main parts of fuel supply systems in modern gasoline powered automobiles are made from polymeric materials. These parts are the fuel tank and intake, fuel pump casing, fuel filter casing, fuel supply lines, injection rail and fuel vapor canister [2]. There is an ongoing popular and scientific discussion about compatibility of those polymeric parts with use of gasoline, containing some part of alcohol. It is well known that some materials, safely used with gasoline with no added oxygenates, deteriorate in environment containing alcohol [3]. Some diaphragms, seals, gaskets and pipes, which contain rubber, swell and change the mechanical properties [4]. Uncoated carbon steel and aluminum alloys are affected by corrosion in ethanol rich environment [5; 6]. Many researchers have tested compatibility of polymeric materials with hydrocarbon fuels or specific test fluids, containing ethanol up to 20 % volume [7-10]. This study focuses on creation of the methodology for evaluation of fuel compatibility of non-elastomer polymeric parts of the fuel system in case of vehicle conversion for E85 use.

Materials and methods

Fuel system endurance is essential for safe and uninterrupted use of automobiles. The essential fuel system polymeric part properties are well defined by Braeckel et al. 2000 [11]:

- Chemical resistance;
- Dimensional stability;
- Mechanical properties;
- Coefficient of thermal expansion;
- Permeability.

Literature studies and the authors' own research revealed that majority of the modern automobiles with gasoline engines, manufactured since 2000, share similar polymeric materials for the key parts of the fuel supply system [2; 11]. Synthetic polymeric parts are made of macromolecules or polymers, consisting of chains of smaller molecules or monomers. The chains of polymers are attracted with each other by hydrogen, ionic, dipole-dipole bonding or by van der Waals forces. The nature of this bonding affects the chemical and physical properties of the polymer. Molecules of liquid fuel may act as solvents on polymeric material, weakening the bonds between the polymer chains and leading to material swelling or even disintegration. The authors collected and identified the material marking codes on the main components of the fuel supply system of the automobiles produced after 2001. In total 36 automobiles of 10 brands were inspected. The results represent the manufacturer's statement of the material choice. The results are summarised in Table 1 and they agree with typical use of polymeric materials in automobile gasoline fuel systems described in literature [2; 12].

Table 1

Polymeric and composite materials in fuel supply system

Code	Name	Fuel rail	Fuel line	Fuel tank	Fuel pump container	Fuel vapor canister
EVOH	Ethylene vinyl alcohol		●	●		
HDPE	High-density polyethylene			●		
PA6	Polyamide 6		●	●		
PA66	Polyamide 6,6					●
PA6 GF30	Glass fiber reinforced polyamide 6	●				
PA66 GF25	Glass fiber reinforced polyamide 6,6	●				●
PA66 GF30	Glass fiber reinforced polyamide 6,6	●				●
PA66 GF35	Glass fiber reinforced polyamide 6,6	●				●
PA12	Polyamide 12		●			
PE	Polyethylene					●
POM	Polyoxymethylene				●	
PP	Polypropylene					●
PVDF	Polyvinylidene difluoride		●			

Markings on some parts are shown in Fig.1. According to the Directive 2003/138/EC, the automotive polymeric parts, having weight more than 100 g, are coded according to ISO 1043-1, ISO 1043-2 and ISO 11469. The purpose of this coding is to facilitate identification of reusable materials of end-of-life automobiles. The coding of polymeric materials does not reveal properties, which are obtained during specific manufacturing processes, such as crystallinity. The coding allows to identify the polymeric material of the fuel system component and assess its principal compatibility with E85. Assessment of compatibility of typical fuel system polymeric materials to high ethanol ration fuel was based on literature studies.

1. Fuel rails

Fuel rails in modern automobiles are made from metal alloy or polymeric material. A typical polymeric material used for manufacturing of fuel rails is a composite – glass fiber reinforced polyamide, marked as PA66GF30, PA6GF25, PA6GF30 or PA6GF35 [3]. The polymeric part of this composite is known as polyamide PA6 (nylon-6) or PA66 (nylon 6,6) [13]. Amide groups in polyamides create hydrogen bonds between the polymer chains. As most polymeric, PA6 and PA66 have crystalline and amorphous regions. Only amorphous regions are directly affected by a solvent, such as water or ethanol. Molecules of the solvent interrupt hydrogen bonds in amorphous regions of PA6, causing swelling and reducing tensile strength [14]. The polar nature of polyamides provides better barrier properties to non-polar fuel components such as hydrocarbons and weaker barrier properties to polar liquids, such as water and ethanol [15]. PA6 will moderately swell till the equilibrium is reached if immersed in ethanol [16]. PA6 also swells if immersed in gasoline or water. The composite PA6GF30 shows lower swell rate in ethanol, gasoline and their blend, comparing to PA6 [3].

Touchet et al. 1982 conducted a research program to test compatibility of polymeric materials with fuel/ alcohol blends. They also determined the effect of materials on fuel blends. Touchet et al. used various fuel/ alcohol blends for the material compatibility study. The highest alcohol ratio was in the test fluid, containing of 80% Texaco Leaded gasoline and 20 % ethanol. The polymeric material properties were determined according to ASTM D-1708. The samples were immersed in sealed test tubes for a period of 28 days in ambient temperature. They found that the glass fiber reinforced polyamide 6 sample exhibited the swell rate 12.3 %, close to the result when pure gasoline was used (10.3 %) Moderate increase of the yield strength (13 %) was observed. The chemical and physical properties of the fuel sample were not significantly affected by presence of polyamide 6 [3].

Baena et al. 2011 tested aggressiveness of a 20 % ethanol 80 % gasoline blend (E20) on various polymeric materials, including PA6GF30. The samples were immersed for 720 h and temperature was controlled at 55±2 °C. PA6GF30 reached equilibrium after 6 days of immersion and mass increase was 6 %. Hardness, thermogravimetric and calorimetric testing revealed no significate effect on sample immersion in E20 test fuel [7].

Fillot et al. 2014 tested PA6 samples in various blends of ethanol, toluene and isooctane, the ethanol fraction varying from 0 % to 100 %. The focus of their research was on permeability of the polymer layer. The results confirmed interaction of polar polymer with polar solvent. It was concluded that PA6 is a suitable material for use in the parts contacting with fuel, containing high proportion of ethanol [15].

2. Fuel lines

Fuel lines are located in more aggressive environment, comparing with other fuel supply system components. Underbody fuel lines are affected by impacts of abrasive chips and stones from the road surface, ice and snow and aggressive effect of salt. Fuel lines in the engine compartment are exposed to vibrations and raised temperature up to 100 ˚C [2]. Some automobile producers use different materials for underbody and engine fuel lines. Polymeric fuel lines are usually designed as multiple layer systems to be able to withstand aggressiveness of external environment and fuel. They also must meet strict requirements of fuel vapor permeability. Typical choice of the spark ignition engine equipped automobile polymeric fuel line material was dual layer polyamide PA6/ PA12. PA12 was used in the outer shell and served as a barrier layer to prevent diffusion and evaporation of hydrocarbon fuel. A more recent approach to multilayer fuel line design is to make the inner and outer layer of the fuel pipe of PA6 or PA12 and include another material to serve as a diffusion barrier for both hydrocarbon and alcohol fuel components. The inner layer of ethylene vinyl alcohol copolymer (EVOH) or polyvinylidene difluoride (PVDF) is used as a barrier [12; 17]. An additional barrier layer ensures that fuel lines meet strict international emission standard requirements. Multiple layer polyamide fuel lines are used in production of Flexfuel automobiles, which are designed to use gasoline-ethanol blend and can be used in automobiles converted for E85 use.

3. Fuel tanks

The automobile fuel storage tank must comply with the existing emission and safety standards, for instance, EC 715/2007. Diffusion and fuel loss rate must not exceed a specific value, currently 2 g per test. As the main function of the fuel tank is to store as much fuel as possible for the given placement in the automobile, it is desirable to make fuel tanks in complex shapes. Use of polymeric materials simplifies this task. Most of the automobiles, produced in Europe since 1980's, have polymeric fuel tanks. The material of choice since introduction of polymeric fuel tanks was high-density polyethnol (HDPE). HDPE is chemically stable in various hydrocarbon and alcohol fuels. The fuel can be safely stored in a HDPE fuel tank but some diffusion and evaporation of fuel occurs. HDPE is non-polar polymer, therefore it is more permeable to non-polar fuels, such as gasoline. Ever stricter emission standards led to development of multilayer polymeric fuel tanks, where an additional diffusion barrier is added. Several techniques are in use – sulphonation or fluorination of the inner layer of the fuel tank or adding a special barrier layer. Typical barrier layers are similar as used in fuel line production and are described in the previous section – PA6 and EVOH. Fluorination provided good barrier properties for hydrocarbons but the layer washed out when alcohol was added in fuel [12]. Fillot et al. 2014 evaluated the barrier properties of PA6 and HDPE in presence of hydrocarbon fuel containing various ethanol contents (E0-E100). Permeability of HDPE was 90 $g\cdot mm\cdot m^{-2}\cdot 24$ h and close to 0 $g\cdot mm\cdot m^{-2}\cdot 24$ h for PA6 when E0 test fluid was used. When tested with fuel containing 85 % ethanol, permeability of both tested materials, HDPE and PA6 was 8-9 $g\cdot mm\cdot m^{-2}\cdot 24$ h [15].

Fig. 1. **Markings on polymeric parts:** 1 – fuel pump container; 2 – fuel line; 3 – fuel vapor canister; 4 – fuel rail.

4. Fuel pump container

Immersed fuel pumps of modern automobiles are multifunctional devices, which may contain the fuel filter, fuel pump, fuel pressure regulator and fuel level indicator. Assessment of full compatibility of the fuel pump unit in case of automobile conversion to use of E85 is a complicated task. Chemical and physical properties of ethanol may lead to premature failure of the elastomer membrane of the fuel pressure regulator, engine brushes or electric contacts of the fuel level potentiometer [4]. Literature studies and observation of various European automobiles allowed concluding that the structural part of the fuel pump unit, the container, is usually made from polyoxymethylene (POM). Dimensional stability and resistance to hydrocarbon and alcohol fuel are the properties, which make POM a popular choice of the immersed fuel pump container and fuel level indicator. The material is compatible with high ethanol content fuel E85 [2].

5. Fuel vapor canister

To limit emissions of fuel vapor, the fuel supply system of modern automobiles with spark ignition engines is sealed. The fuel vapor is accumulated in the canister. The canister is filled with carbon pellets, which adsorb fuel. The accumulated fuel is removed from the canister periodically, according to the engine control module strategy. The fuel vapor canister casing is typically made of polymeric or composite materials. While inspecting the markings on fuel vapor canisters, the authors observed greatest variation of material choice among all checked fuel system components. Fuel vapor canister casing is usually made of single layer PE, PP or PA66, multilayer PE/ PP or polyamide and glass fiber composite PA6GF25, PA6GF30 or PA6GF35. A fuel vapor canister, made of single layer PP might be unsuitable for use with E85 fuel, as Touchet et al. 1982 found it affected by alcohol fuel. Subsequent swell and loss of strength in presence of ethanol or methanol was found [3]. The authors found that fuel vapor recycling control valve casings in all inspected automobiles were made of PA6GF30 or PA6GF35, which are considered compatible with E85.

Results and discussion

Components of automobiles, which weigh more than 100 g and are made of polymeric materials, are marked to identify the type of material. This marking can be used to check compatibility to E85 fuel of the automobile fuel system components, which are made from polymeric materials. The authors collected the marking data of the fuel delivery system polymeric parts from various automobiles with spark ignition engines, built from 2000 to 2015.

Fuel rails, linings and immersed fuel pump casings were found generally compatible with E85. Fuel tanks, made of single layer HDPE, might have special treatment, such as fluorination, which will be washed out by E85. HDPE fuel tanks with washed out fluorination barrier will be compatible with E85 but can cause increased permeability of gasoline. Fuel tanks, made of HDPE and multiple layer barrier polymeric material, were found compatible with E85. Fuel vapor canister casings, which are made of PP, might show increased swell and loss of strength. Other polymeric and composite materials, typically used for fuel vapor canister casings, were found compatible with E85. Efficiency of E85 adsorption and recycling in gasoline fuel vapor canisters is subject to future work.

Conclusions

1. Materials of polymeric and composite parts of the spark ignition engine fuel supply system can be identified by finding standardized marking.
2. Composite fuel rails are typically made of glass reinforced polyamide PA6 or PA66 and this material is compatible with E85 fuel.
3. Fuel lines must be inspected in full length, as different materials can be used according to the position in the automobile.
4. Multiple layer polyamide fuel lines of modern spark ignition engine equipped automobiles can be considered compatible with E85 fuel.
5. Basic material of a modern automobile fuel tank – high density polyethylene (HDPE) is compatible with E85 fuel.
6. Fuel tanks made of HDPE with polymeric barrier layers PA6 or EVOH can be considered compatible with E85 fuel.
7. The fluorination barrier layer of fuel tanks might be washed out in E85 environment and increased permeability of gasoline can occur.
8. Immersed fuel pump container material – polyoxymethylene (POM) is compatible with E85 fuel.
9. Fuel vapor canisters, which are made of polyethylene or polyamide polymers and polyamide/ glass fiber composite, can be considered compatible with E85 fuel.
10. Polypropylene single layer fuel vapor canisters might be unsuited to use with E85 fuel.

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