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COMPATIBILTY STUDY OF THERMOPLASTICS IN RON97 GASOLINE BLENDED WITH ETHANOL

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ABSTRACT

This paper investigates the compatibility of three types of thermoplastic: low density polyethylene (LDPE), high density polyethylene (HDPE) and polypropylene (PP) with ethanol blended gasoline. These polymeric materials have been applied as components in automotive fuel system and the material integrity is important. The commercial RON97 unleaded gasoline were blended with 5, 10 and 20 vol.% of ethanol to make the fuel blends. The plastic specimens were immersed in the fuel blend for 14 and 28 days at ambient conditions. Baseline tests using neat gasoline without ethanol were included for comparison purpose. The weight change, tensile strength and hardness properties were measured to assess the impact of the immersion tests. Results showed that the immersed specimens showed similar change of colour but no swelling was observed. Greater percentage of ethanol contributed to greater mass gain and incremental loss of tensile strength and hardness.

Keywords: ethanol blended gasoline, polymer, immersion tests, mechanical properties.

INTRODUCTION

Nowadays, additives are typically added to the fossil fuel to improve its anti-knock property and fuel efficiency. One of the commonly used additives is the ethanol alcohol which acts as oxygenate [1]. The oxygenate boosts up the octane rating which results in better fuel efficiency and gas mileage. By blending ethanol to the gasoline, a greater mass of fuel can enter the engine cylinder since the ethanol blend increases the vaporization enthalpy, hence reducing the temperature in the intake header of the engine [2]. In countries such as USA and Brazil, ethanol has been used extensively as additive blended in commercial gasoline to create ethanol blended gasoline, which can vary from 5% of ethanol (E5) to 20% (E20) of ethanol. Engine performance results showed that ethanol blend improved the thermal efficiency at lower loads [3]. Most engine performance results showed that the E5 and E10 blends gave the best improvement in energy efficiency [4].

Historically, ethanol is not the primary choice of automotive fuel because of the economic reasons compared to fossil fuel. Ethanol becomes an attractive choice as a renewable energy source since it can be converted chemically or biologically from plants such as corn or sugar cane when the fossil fuel becomes increasingly expensive or depleted. However, certain aspects of the ethanol blended fuel have to be used with caution. Ethanol alcohol is a solvent which is incompatible with some polymers, elastomers and plastic composites. Ethanol molecules can react with the polymers, which over time result in swelling and breaking down the carbon-carbon bonds in the hydrocarbon chains. This leads to loss of chemical structure and may be structurally fatal as the material degradation is irreversible. Kass *et al.*[5, 6] found that the ethanol reformulated gasoline will dissolve the polymers, by stripping off the base polymer or any additives used as plasticizer, hence lowering the coupling property of the polymers. Dhaliwal *et al.* [7] reported that the neoprene and nitrile elastomers were significantly degraded after 21 days of immersion in E10 blend. Another issue is related to the hygroscopic nature of ethanol, in which it attracts water and leads to water accumulation once the phase separates out. This poses a serious corrosion threat to any contacting metallic parts such as gasoline tank, especially combined with sodium chloride salt. The compatibility of various plastic and elastomer materials have been studied by various researchers [5-8]. Jones *et al.* [8] conducted a comprehensive study on the effects of 20% ethanol reformulated gasoline on a number of plastic and elastomer materials used in automotive fuel system components. 10 types of materials and 3 types of fuels were tested for 18 weeks at an elevated temperature. Mixed results were reported: Acrylonitrile butadiene styrene (ABS) disintegrated completely while polyetherimide (PEI) showed good intact of tensile properties. A compatibility study by Dhaliwal *et al.* [7] focused on the effects of different percentage (5%, 10% and 15%) of ethanol in fuel mixture on polymer and elastomer samples. Different materials were observed to respond differently depending on the ethanol content in the fuels. The tensile properties of elastomer materials were affected more significantly than plastic materials. Jones *et al.* [8] reported that the tensile strength of polymer samples after blended fuel immersion decreased significantly while the impact strength increased.

The implementation of Malaysia's National Biofuel Policy 2006 has focused on the development of processed palm oil as biodiesel for 5% blend as the renewable energy source [9]. Nonetheless, the potential use of ethanol cannot be ignored as the current worldwide trend of blending ethanol with the gasoline as the reformulated fuel. Most automotive components were made of metallic materials in the earlier production, but were gradually replaced by light weight polymers in recent development. For example, the average vehicle weight

using iron steel has been decreased from 70% in 1990 to 61% in 2001 [10]. In the present work, the compatibility of polymer with ethanol blended gasoline in local market was investigated. Three types of thermoplastics: low density polyethylene (LDPE), high density polyethylene (LDPE) and polypropylene (PP) were immersed for 28 days at 25 °C in fuel blends with varying ethanol content from 5% (E5), 10% (E10) to 20% (E20). The changes in physical and mechanical properties of the immersed specimens were compared in order to assess the effects of ethanol blended fuel to the polymer components in fuel system.

METHODOLOGY

Specimen preparation

Three types of thermoplastic pellets: low density polyethylene (LDPE), high density polyethylene (HDPE) and polypropylene (PP) were used as the specimen. All specimens were produced using the compression moulding machine (Carver's Monarch Hydraulic Lab Press), as per ASTM D4703 [11]. Compression moulding is a way to form homogeneous plastic parts using pressure and heat. The polymer granules are placed in a heated mould cavity while fully enclosed and pressed by the clamp, followed by curing at specified cooling rate. After the mould was open to remove the specimens, they were inspected for discolouration, sink mark and shrink holes. Five specimens per material per fuel were prepared for the physical and mechanical tests, with One set of specimens per material were used as baseline which was not subjected to any immersion.

Test parameters

The gasoline used was unleaded RON97, purchased from a nearby petrol station in Bandar Sri Iskandar, Perak. The ethanol (C_2H_5OH) used was laboratory grade. The properties for the fuels are listed in Table-. Different fuel blends E5, E10 and E20 were prepared by mixing the two fluids according to 5%, 10% and 20% volume fraction, respectively.

Table-1. Test matrix.

Property	Value
Base fuel	RON97 (C_8H_{18})
% vol. ethanol	0, 5 (E5), 10 (E10), 20 (E20)
Specimen type	LDPE, HDPE, PP
Immersion duration	14, 28 days
Test conditions	25°C, 1 atm.
Measurement techniques	Visual inspection, immersion, tensile test and hardness tests

Immersion test

Three specimens, made in tensile dogbone shape, from each thermoplastic type were conditioned, dried and weighed before immersing in the fuel blend for up to14 and 28 days at room temperature. The specimens of the same material type were hanged and immersed in a clear bottle, in which they were monitored for colour and mass change. All immersed specimens were wiped dry before being weighed in an analytical balance, to a resolution of 0.001 g. A repetition of five readings was taken and the mean was recorded. The assessment of the physical appearance and the colour change were made to the immersed specimens in order to study the effect of different fuel blends to the materials. Comparison were also made with specimens immersed in pure gasoline.

Hardness test

Indentec Rockwell Hardness Tester in HRR scale with ½" steel ball indenter and 60 kg load was used for the hardness measurements. Measurement points were made at the clamping ends of the tensile specimens so that the indentations made will not affect the subsequent tensile testing. The hardness of the specimen (per material per fuel) was measured before and after immersion in the blended fuel. The measurements were repeated three times at different locations to obtain the mean, as per the procedure in ASTM D785 [12].

Tensile testing

Zwick Roell Universal Testing Machine (UTM) was used for the tensile testing. For each type of materials and fuels, the tensile strength was measured for each set of specimens before and after the immersion. The tensile tests were performed as per ASTM D638 [13].

RESULTS AND DISCUSSION

Visual inspection

Visual inspection was performed to assess the colour change of the immersed specimens in different blended fuel mixtures after 14 and 28 days. All specimens showed colour change from translucent to yellowish after 14 and 28 days of immersion, with the latter appeared to be more yellowish than the former. By cross-comparing with different blended fuels: gasoline, E5, E10, and E20, the colour change showed that the fuels added with ethanol or without ethanol resulted in almost similar colorization effect. LDPE specimens appeared to be more affected while PP specimens were less affected to colour change. For HDPE, E10 and E20 specimens showed more yellowish tinge than E5 and gasoline specimens. For PP, only pale yellowish tinge was observed after 28 days of immersion. All specimens were found in good physical appearance without cracks, swelling or roughness. The lack of swelling somewhat indicated the poor solubility between the specimens and ethanol alcohol.

Weight change

In Figure-, all thermoplastics specimens showed mass gain after 28 days of immersion. Specimens immersed in pure gasoline displayed the least percent of mass gain (<3%). The percent of ethanol content affected

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the mass change. It appeared that the higher percent of ethanol in the fuel blend, the higher percent of mass gain. E20 specimens showed 8% mass increment after 28 days.

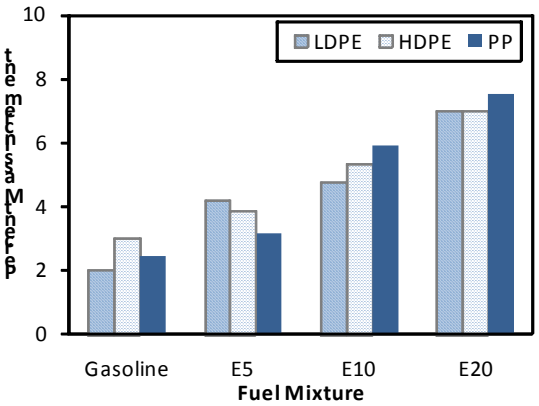


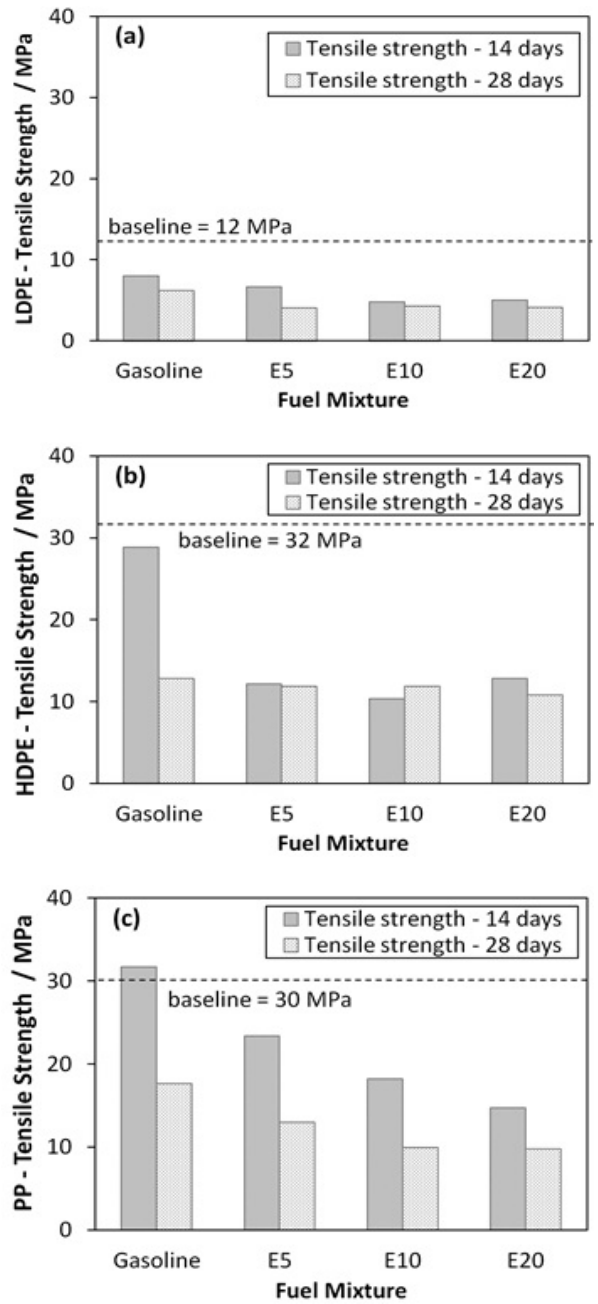
Figure-1. Percent mass increment for LDPE, HDPE, and PP after 28 days of immersion.

Tensile strength results

Figure-(a) to (c) show the effects of varying ethanol contents and immersion duration on tensile strength for three types of thermoplastic specimens immersed in fuel mixtures. For LDPE specimens in Figure-(a), the tensile strength results after immersion showed reduction in the range of 33–66% compared with the baseline value (12 MPa) of untreated specimens. Increasing the ethanol content caused a downward trend of tensile strength for both 14 and 28 days of immersion, with tensile strengths of E10 and E20 specimens reduced by more than half. For HDPE specimens in Figure-(b), all measurements showed more than 60% reduction in tensile strength except for the 14-day specimen immersed in pure gasoline, when compared with the baseline value (30 MPa). Fuel mixtures E5 to E20 were detrimental to the loss of tensile strength; however the length of immersion did not aggravate the degradation. Figure-(c) shows the tensile strength results for PP specimens that trend downwards with increased ethanol content and immersion duration. Comparing with the baseline value (30 MPa) of untreated specimens, the drop of tensile strength of immersed specimens was recorded in a range of 22–67%. An increase in the ethanol content caused an incremental drop in tensile strength, while an increased length of immersion worsened the degradation.

Hardness results

Figure-(d) to (e) shows the Rockwell Hardness Scale R results in varying ethanol contents and immersion duration for three different types of thermoplastic specimens immersed in fuel mixtures. For LDPE specimens in Figure-(d), all the hardness results dropped about 20 – 30% when compared with the baseline value (50 HRR) of untreated specimen. The increase in the ethanol content and the length of immersion did not greatly aggravate the loss of hardness, showing only slight difference between specimens. The hardness results in Figure-(f) for HDPE specimens display an almost flat-line trend, with the drop in specimen hardness ranging from 9 to 20% when compared with the baseline value (58 HRR). Similar to LDPE results, there was slight reduction in hardness values when the duration of immersion was increased. Figure-(e) shows the hardness results for PP specimens, which trend slightly downwards between the specimens. The reduction in hardness was noted in the range of 5–20%, comparing to the baseline value (99.8 HRR). Increasing the ethanol content and the length of immersion caused slight fall in hardness values.



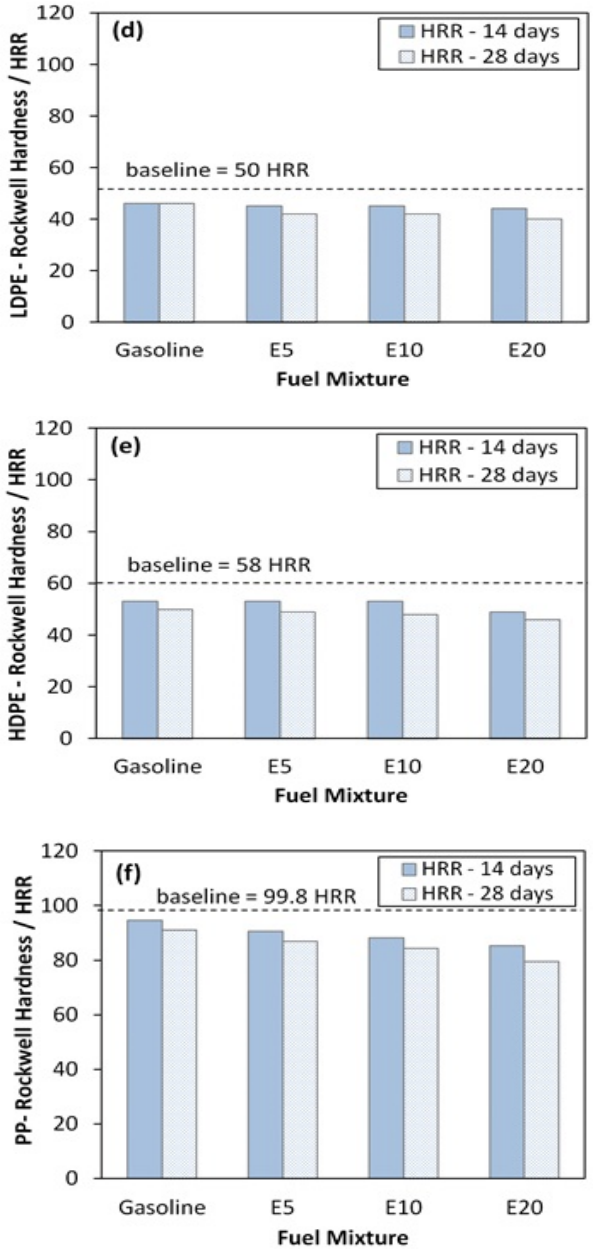


Figure-2. (a)–(c) Tensile strength results; (d)–(e) Rockwell hardness results for LDPE, HDPE, and PP after immersion in varying fuel blends.

The overall percent reduction of tensile strength and Rockwell hardness results compared to baseline after 28 days of immersion were summarized in Table-.

Table-2. Percent reduction of tensile strength and hardness results after 28 days of immersion.

Fuel Blend		Pure Gasoline	E5	E10	E20
LDPE	% reduction in Tensile Strength	48.1	66.0	64.1	65.6
	% reduction in Hardness	20.7	27.6	27.6	31.0
HDPE	% reduction in Tensile Strength	60.0	63.0	62.9	66.3
	% reduction in Hardness	13.8	15.5	17.2	20.7
PP	% reduction in Tensile Strength	41.2	56.8	66.9	67.4
	% reduction in Hardness	8.7	12.9	15.5	20.3

CONCLUSIONS

The present work studies the compatibility of three types of thermoplastics (LDPE, HDPE, PP) immersed in varying percent of ethanol in RON97 unleaded gasoline. The work is important as the findings revealed that the properties of thermoplastics were greatly affected by the ethanol percentage and the length of immersion time. The main conclusions drawn from the current work are as follows:

- All immersed specimens showed similar colour change to yellowish tinge. No physical crack or swelling was observed.
- All immersed specimens experienced mass gain. Higher ethanol content in fuel blend contributed higher mass gain up to 8%.
- All specimens showed an incremental loss in tensile strength and hardness by creasing the ethanol content and the immersion duration. The tensile strength and hardness reduced as much as 60% and 20%, respectively.

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