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The Effect of Methanol-Gasoline (M20) and Ethanol-Gasoline (E20) Blends on Material Compatibility

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ABSTRACT - Alcohol has the potential to be used as an alternative to fossil fuels to reduce total emissions from spark-ignition (SI) engines. The impact of a mixture of 20% methanol and ethanol in gasoline on the compatibility of Ethylene Propylene Diene Monomer (EPDM) and polyamide materials, which are used as fuel hoses in SI vehicles, is presented in this study. The immersion test methodology was employed to study the influence of both types of alcohol on gasoline blend to compatibility properties i.e., hardness and weight change. Based on the result, EPDM and polyamide materials have different characteristics of material compatibility with E20 and M20. Tests on M20 and E20 fuel samples on EPDM material show a higher effect on hardness by 5-9% than pristine gasoline. Additionally, there was no change in the weight of the polyamide material in the RON 90, E20, and M20 test samples. However, there was a change in the hardness of the polyamide material by 6-11% in RON 90, E20, and M20 fuels. Moreover, there was no change in the FTIR spectrum, indicating that there was no dissolution of the EPDM and polyamide materials into the test fuel for 6 weeks of immersion.

Keywords: Ethanol, methanol, compatibility, EPDM, polyamide.

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INTRODUCTION

Oxygenated fuel is one of the promising alternative fuels to lower exhaust emissions. One of the oxygenate compounds that have been studied and have the potential to be widely applied in alcohol (Canakci et al., 2013; Masum et al., 2015a, 2015b). Alcohol has a high octane number (*Research Octane* Number, RON), high oxygen content, sulfur-free, and low-carbon. Based on these characteristics, there are currently many studies exploring methanol and ethanol as substitute fuels for gasoline (Awad et al., 2018; Yusri et al., 2017). Methanol has a RON value of 129-134, Oxygen content of 49.9 %-mass, a vapor pressure of 32.2 kPa, and a Lower Heating Value (LHV) of 26,1 MJ/kg. On the other side, ethanol has a RON of 109, an Oxygen content of 34.7 %-mass, a Vapor pressure of 17.2 kPa, and a Lower Heating Value (LHV) by 27.0 MJ/kg (Aghahossein Shirazi et al., 2019; Calvin et al., 2022). With a high RON value, the addition of methanol and ethanol can also be used as mixed components to increase the RON of gasoline (Octane Booster). In addition, the oxygen content in methanol and ethanol also has the potential to produce perfect combustion resulting in reduced emissions of carbon monoxide and unburned hydrocarbons (UHC). But, the percentage of mixing methanol and ethanol as gasoline blended fuels is still being researched and explored due to a concern about the resulting characteristics of having to adapt to the vehicle engine technology currently on the market (Sugiarto et al., 2019, 2020).

In general, adding methanol and ethanol results in a linear increase in octane numbers and oxygen content (Calvin et al., 2022). The use of ethanol-gasoline and methanol-gasoline fuel blends causes to decrease in CO and unburned HC emissions significantly, this is due to improving combustion process as a result of oxygen content in ethanol and methanol (Canakci et al., 2013). However, some studies show that methanol and ethanol experience an azeotropic effect (mixing is not ideal) with a gasoline vapor pressure at low concentrations. Methanol and ethanol can affect vapor pressure and gasoline distillation curves, thus forming a non-ideal curve due to polarization in the equilibrium of fuels. The highest vapor pressure is produced in the 10-20% methanol/ethanol concentration range in gasoline (Abdurrojaq et al., 2021; Aghahossein Shirazi et al., 2019). Therefore, although methanol and pure ethanol have a lower vapor pressure, mixing them with gasoline increases steam pressure compared to pristine gasoline. Therefore, the percentage of methanol and ethanol used in gasoline must-produce fuel characteristics that can produce optimal performance and not negatively affect metal and non-metal materials in engine component systems (Durbin et al., 2016; Vyas et al., 2013).

Some research shows that the use of methanol and ethanol as a mixture of gasoline in the automotive sector requires the selection of metal and non-metal materials whose durability is appropriate. Methanol and ethanol can interact, thus severing the bond between the resin and fiberglass from the fuel tank, causing the leak, resulting in the resin material attached to the valve and other engine parts due to deposits and blockages in the entrance valve. Another problem that may arise is the corrosive nature of metal fuel tanks due to the very high affinity of methanol and ethanol to water. Ethanol mixture 20% (E20) causes many problems in various plastics, rubbers, and metal components. Some polymer materials such as Nylon-6, Nylon-66, PET, and Polyetherimide (PEI) showed the same with 3 fuel mixtures including 50/50 toluene-isooctane, E10, and E20 (Durbin et al., 2016; Vyas et al., 2013). Other materials compatible with the E10 fuel mixture include Delrin, which should not be used Neoprene Polymers, Nitrile, or HNBR that are not compatible with E10 (Turner et al., 2013; Wouters et al., 2020).

Currently, research on the effect of methanol and ethanol mixtures on the compatibility of non-metallic materials of Ethylene Propylene Diene Monomer (EPDM) and polyamide is still limited. Identification of the material of the parts was done by FTIR and DSC for non-metal parts and by XRD and XRF for metal parts (Anggarani Riesta, Cahyo S. Wibowo, 2015). As one of the building materials of fuel lines in vehicles, the effect of methanol and ethanol on the compatibility of EPDM and polyamide materials is significant to be explored. Therefore, this study presents the effect of a mixture of 20% ethanol (E20) and 20% methanol (M20) on gasoline on the compatibility of EPDM and polyamide materials. The test refers to SAE J1748 2018-08 method for compatibility of polymer material properties exposed to fuel mixtures/oxygenate substitutes with additives.

METHODOLOGY

Preparation Fuel Test

The gasoline used is a type of commercial gasoline with RON 90. Methanol and ethanol are used as a type of fuel grade that comes from one of the producers in Indonesia. Fuels of 20% methanol (M20) and 20% ethanol (E20) in RON 90 gasoline is carried out on a volume basis and in cold conditions to minimize evaporation. After mixing and then homogenizing, the fuel is stored in the refrigerator at a temperature of 0-4 ^{o}C.

Preparation of Non-Metal Materials

Two types of non-metal materials as fuel lines in vehicle engine combustion systems, EPDM and polyamide are used in this study. The two types of fuel lines are obtained from one of the vehicle manufacturers in Indonesia. Both materials were identified with FTIR (Fourier Transform Infra-Red

Spectroscopy) with ASTM E1252-13 test method and Transition Temperature Analysis with DSC (Differential Scanning Calorimetry) with ASTM D3418-15 test method. Hose material is cut precisely by adjusting the area of the immersion container. Hoses that are already in small size are then dried and weighed to gain the initial weight of the specimen (the test is carried out outside the LEMIGAS).

Immersion Test

Material compatibility testing is conducted for 6 weeks or ±1000 hours of immersion with a change of test fuel every 1-week interval. Immersion is conducted constantly at 55 °C ± 2 °C in dry baths. Measurement of weight and hardness after drying the material for 60 minutes at a temperature of 40-50°C. Analysis of material changes is done by testing the hardness and weighing of material weights each week. This compatibility test is also calculated with the F test (statistical math formula) to see the movement of material changes each week with the hypothesis that if F calculates lower than the F table then the material change has reached equilibrium compared to the measurement in the previous week. The immersion test refers to the SAE J1748 2018-08 method "Methods for Determining Physical Properties of Polymeric Materials Exposed to Hydrocarbon Fuels or Their Surrogates and Their Blends with Oxygenated Additives".

RESULTS AND DISCUSSION

The characteristics of methanol and ethanol gasoline in Table 1 have differences in the research octane number, density, boiling point, vapor pressure, and oxygen content. Methanol has the highest octane number when compared to gasoline and ethanol. Contrarily, gasoline has the lowest density compared to ethanol and methanol. The characteristic of vapor pressure in gasoline is the lowest, the addition of alcohol to gasoline mixtures increases the vapor pressure by 19 kPa for methanol by 20% and 6 kPa for ethanol by 20%. While M20 and E20 have oxygen content obtained from methanol and ethanol so it is believed to improve combustion and also make emissions cleaner compared to gasoline. (Abdurrojaq et al., 2021).

Identification of material hose with FTIR in Table 2 shows that hose has EPDM material composition (Ethylene Propylene Diene Rubber) with six spectrums of wavelength compared to reference data, and the other one hose has a polyamide material composition of fourteen wavelength spectrum. Transition Temperature Analysis with DSC to measure enthalpy changes due to changes in the physical and chemical properties of a material as a function of temperature or time and can identify and determine the characteristics of matter.

Table 1
Fuel characteristics gasoline 90, M20 and E20

No	Test Parameter	Unit	Method Test ASTM	Fuel Characteristic		
				Gasoline 90	M20	E20
1	Octane Number	RON	D2699	90,1	98,9	97,5
2	Oxygen Content	% m/m	D6730	0,0	9,8	6,9
3	Vapor Pressure	kPa	D5191	59,0	79,7	65,0
4	Density (T: 15ºC)	kg/m³	D4052	725,4	737,4	738,5
5	Copper Strip Corrosion	Merit	D130	1a	1b	1a
6	Mercaptan Sulphur	%-mass	D3227	<0,0003	<0,0003	<0,0003
7	Methanol Content	%-mass	D5845	0	20,1	0
8	Ethanol Content	%-mass	D5845	0	0	19,9
9	Water Content	ppm	D6304	39	81	194

The first material with the composition of the material is EPDM and the second material is Polyamide with each tested with 3 fuels and measured every week to see the rate of Change of the material. The rate of change in the EPDM material hose is shown in Figure 1. Changes in EPDM material weight indicate a considerable decrease for the M20, E20, and RON 90. The result of material immersion in E20 is a change in weight and hardness that is higher than M20 and RON 90. EPDM material undergoes a 29% weight change in E20 fuel. While the immersion in M20 and RON 90 fuels causes weight changes of 20% and 18%. The results showed that the use of 20% ethanol can cause an 11% increase in weight change when compared to pure gasoline. Conversely, on the M20 fuel, there is a no different change compared with pure gasoline.

Table 2
Analysis wavelength spektrum FTIR and transition temperature

No	Sample	Results	Wavelength (cm⁻¹)	Reference	Transition Temperature
1	H1	EPDM	2954; 2924; 2853; 1462; 1377; 721	ISO 465 : 2010 (E) Table B.6 Figure B.10	T_{glass} = -55.17°C
2	H2	Polyamide	3307; 2920; 2852; 1638; 1540; 1465; 1420; 1374; 1262; 1190; 1158; 1055; 938; 723	Hummel 2189	$T_{melting}$=182,70°C

In general, EPDM materials experienced increased hardness in each test fuel. This increase occurs on each measurement week as can see in Figure 1. In the 6th week of measurements obtained adjacent results from all three fuels. In contrast to the results of weight measurements, the M20 fuel-soaking fuel hardness measurement produces the highest change with a value of 30%. Meanwhile, E20 and RON 90 fuels caused a change in hardness in EPDM materials

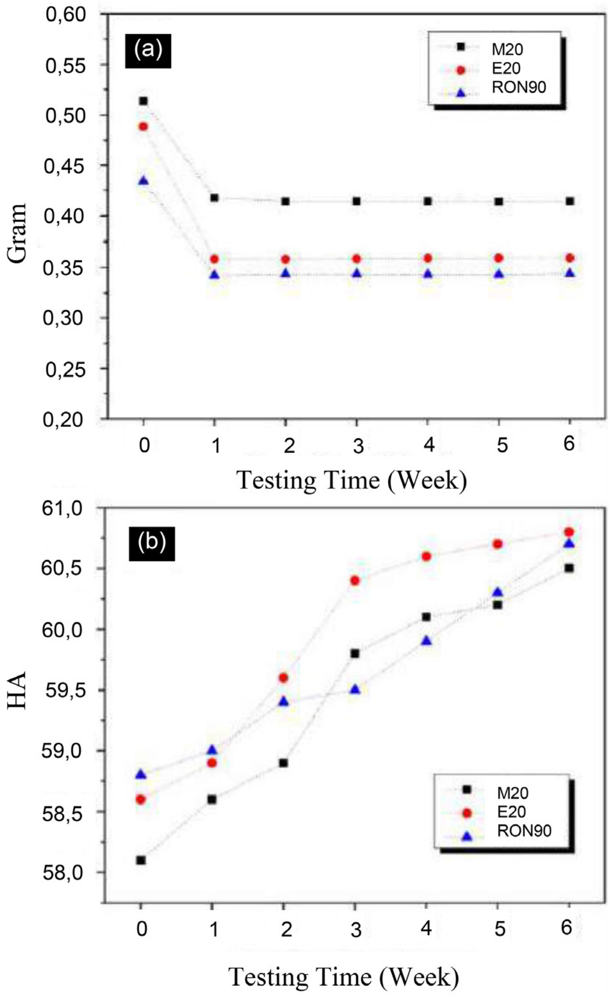


Figure 1
(a) Weight change graphic - EPDM,
(b) Hardness change graphic - EPDM

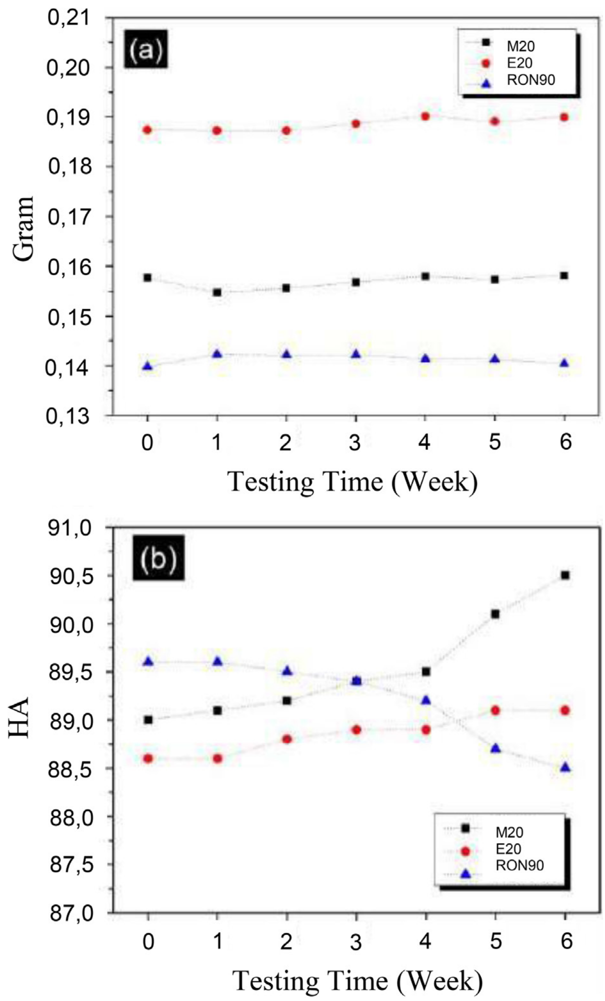


Figure 2
(a) Weight change graphic - polyamide,
(b) Hardness change graphic - polyamide

with values of 26% and 21%. The results showed that the use of 20% methanol and ethanol had a change in hardness of 5-9% higher than that of pure gasoline. EPDM rubber absorbs the fuel alcohol-gasoline mixture through the pores, then the drying process evaporates the remaining fuel in the pores which keep repeating every week, causing the material to swell and shrink during the testing process.

Polyamide materials have different changes to EPDM. In Figure 2 it is seen that there is no change in the weight of the polyamide material in the ron 90, E20, and M20 fuels. Meanwhile, there was a change in the level of polyamide material hardness during the 6-week immersion time. The highest hardness change was produced by polyamide material soaked with M20 fuel, at 11.5%. E20 fuel causes a 6% violent change in polyamide material. While, on RON 90 fuel, as a control fuel, there was a 10% change in hardness in polyamide material. Figure 2 These results showed the polyamide material was compatible with RON 90, E20, and M20 fuels on the weight parameter, but there was a change in the hardness parameter.

The graphic in Figure 3. indicates a percent value change from the beginning of the measurement to the end of the sixth week of measurement. EPDM materials have a change effect with the immersion method much greater than polyamides. EPDM material undergoes stated degradation with a decrease in weight and a 20-30% increase in hardness. Polyamide materials with E20 immersion fuel have the smallest changes between M20 and RON 90 fuels. Figure 4 shows the FTIR spectrum of pure RON 90 fuel compared to the fuel used to soak EPDM and polyamide. Test results showed the transmission produced by the fuel before and after testing was still identical, clustered, and did not undergo any shift or expansion of the spectrum. These results showed no

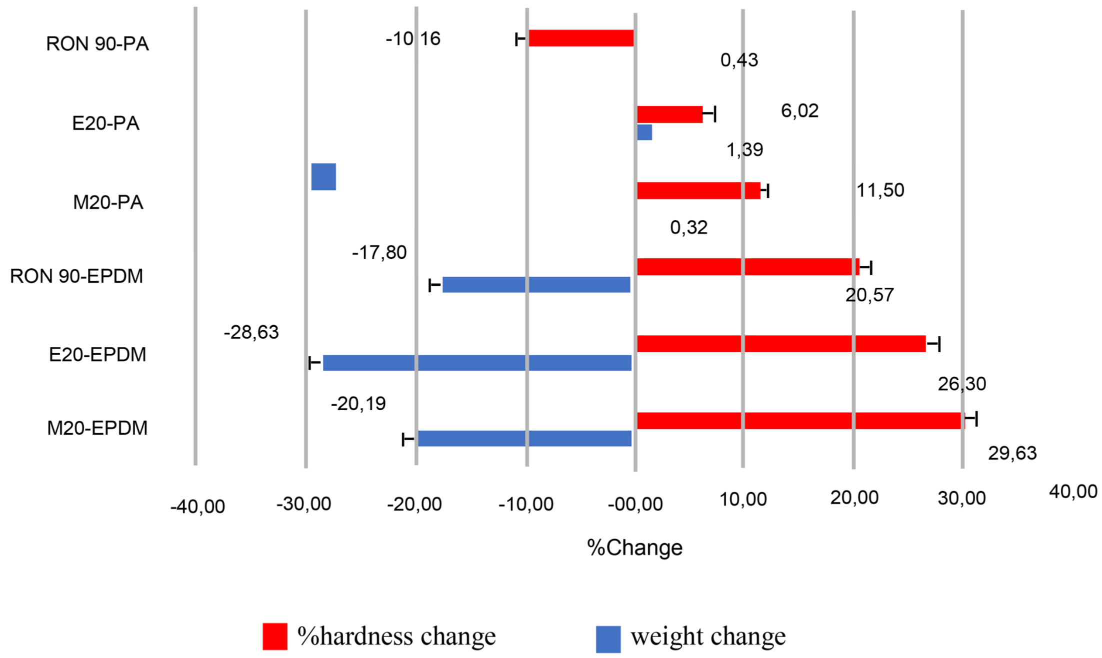


Figure 3
Change graphic of materials non-metal

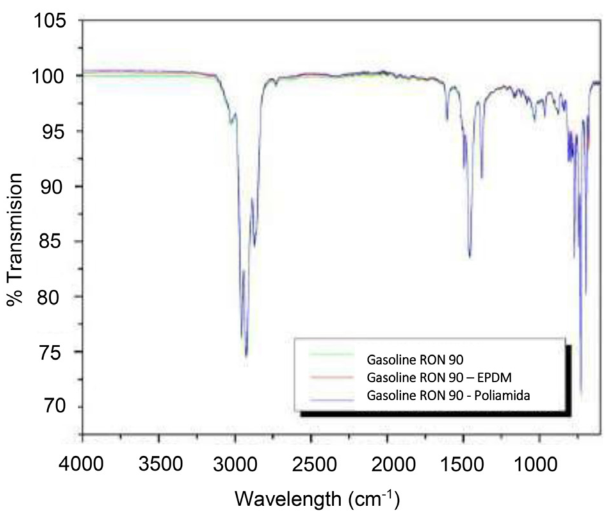
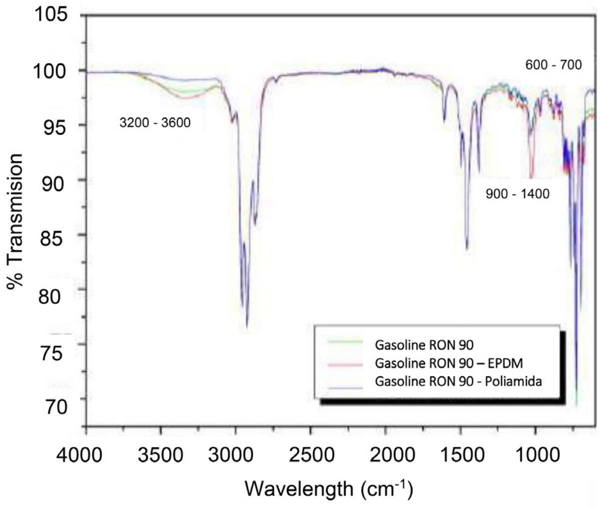


Figure 4
Spectrum changes in FTIR transmission
fuels gasoline RON 90

solvent detected in EPDM and polyamide materials during 1000-hour immersion testing on the fuel. The composition of the fuel function group was also not changed by FTIR detection. Spectrum graph FTIR of M20 fuel in Figure 5. Early fuel shows have an OH group bond with a single bond visible from the curves at wavelengths 3200-3600 cm^{-1}. Fuel after immersion indicates the dilation of the spectrum curves at wavelengths 3200-3600 cm^{-1} indicates that a single bond OH group increases which indicate that water vapor joining the alcohol compounds in the fuel mixture increases due to the appearance of hygroscopic properties of the alcohol. This also happens with the E20 fuel seen in Figure 5. The spectrum at wavelengths 3200-3600 cm-1 appears deeper curves wave indicating the presence of OH groups and in fuel after immersion of the spectrum the presence of OH groups is increased because the hygroscopic nature of alcohol affects E20 fuel.

In immersion testing for 6 weeks or 1000 hours is calculated with a Test F for each material and fuel. To monitor the significance of test F is required to compare it with Table F which refers to the SAE J1748 2018-08 Methods for Determining Physical Properties of Polymeric Materials Exposed to Hydrocarbon Fuels or Their Surrogates and Their Blends with Oxygenated Additives. In this study, 3 test specimens (in immersion containers) were conducted for every 1 test (1 fuel for 1 type of material) and 3 measurements were taken for each specimen. Then the value of F used in Table F is 5.14.

This test obtained F calculate for each test (1 fuel for 1 type of material) can be seen in Table 3. Values smaller than 5.14 are EPDM materials on all types of M20, E20, and RON 90 test fuels. That states that equilibrium has been achieved and the process of material change has tended to be the same. In contrast, polyamide material has not been declared equilibrium in each specimen because the value of F calculate is still greater than F Table.



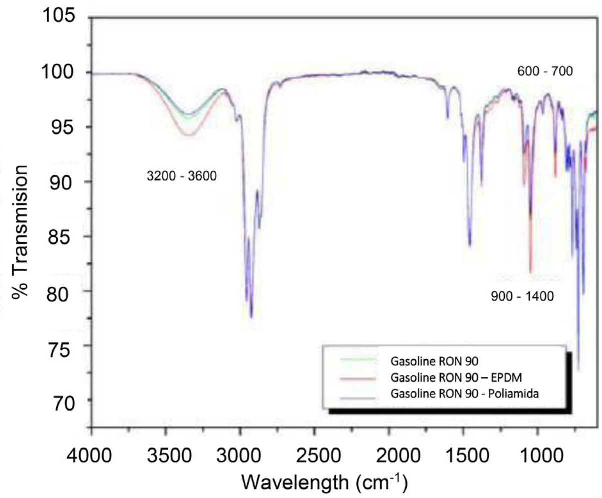


Figure 5
Spectrum changes in FTIR transmission mixed gasoline fuel with 20% ethanol and 20% methanol

CONCLUSIONS

In summary, the effect of 20% methanol (M20) and ethanol (E20) in gasoline on the compatibility of EPDM and polyamide materials have successfully been carried out in this study. Here, both test sample materials, EPDM and polyamide, have different characteristics of material compatibility with E20 and M20. Based on the results, M20 and E20 fuel test samples show that

Table 3
F table value

F Table	F Calculate					
5,14	M20 (EPDM)	E20 (EPDM)	RON 90 (EPDM)	M20 (Polyamide)	E20 (Polyamide)	RON 90 (Polyamide)
	0,027097	0,025608	0,272253	12,0792816	11,94391842	12,7760935
Hasil	< F Tabel	< F Tabel	< F Tabel	> F Tabel	> F Tabel	> F Tabel

EPDM material has a higher effect on hardness changes by 5-9% compared to pristine gasoline. However, there was no change in the weight of the polyamide material in the RON 90, E20, and M20 fuel tests. Furthermore, there is a change in the hardness of the polyamide material by 6-11% in the RON 90, E20, and M20 fuel tests. It was clear that polyamide material is more compatible with exposure to E20 and m20 fuels compared to EPDM. Moreover, there was no change in the FTIR spectrum, indicating that there was no dissolution of the EPDM and polyamide materials into the test fuel for 6 weeks of immersion.

EPDM hose undergoes physical changes over a long period when exposed to a mixture of gasoline and alcohol, then the use of EPDM hose can be placed on the part that is slightly in contact with the fuel blends. Polyamide is one of the materials that can be prioritized if the fuel used is a mixture of gasoline and alcohol because its durability can be very long.

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GLOSSARY OF TERMS

Symbol	Definition	Unit
ASTM	American Stardard Testing and Material	
DSC	Differential Scanning Calorimetry	ºC
EPDM	Ethylene Propylene Diene Rubber	
E20	Mixed fuel gasoline with 20% ethanol	%v/v

FTIR	Fourier Transform Infra-Red Spectroscopy	cm^{-1}
HNBR	Hydrogenated Nitrile Butadiene Rubber	
M20	Mixed fuel gasoline with 20% methanol	%v/v
PA	Polyamide	
RON	Research Octane Number	
RON 90	Gasoline fuel with content the octane number value of 90	
SAE	Society of Automotive Engineers	

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