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Comparative Study of the Effects of Diesel and Biodiesel Over POM, PPA and PPS Polymers Used in Automotive Industry

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Abstract

Energetic needs and environmental concern are causing the evolution of fuels. Biofuels have started to partially replace non-renewable fuels. Among them, Biodiesel has occupied an important place on automotive industry. In the other hand, polymeric materials have substituted metals in some automotive components. Sometimes they are in direct contact with fuels, and then compatibility between polymers and fuels is essential. In this study, the compatibility of three different engineering polymer families, POM, PPA and PPS, is assessed with diesel and SME biodiesel. Polymer samples were exposed to fuel for a 1008h period at 120°C, simulating automotive extreme conditions. Mechanical properties of the specimens were evaluated at different periods of time. Differences on effects of biodiesel and diesel were assessed for the different families and it was found that the effect of biodiesel and diesel over the analyzed polymers is the same for both cases: the mechanical properties are slightly modified.

Keywords: Diesel; Biodiesel; Polymers; Metals

Introduction

Substitution of metals by engineering polymers is a common practice in automotive industry. Depending on the function of the selected automotive components, the polymers must meet some requirements such as chemical resistance, heat resistance, retention of mechanical properties, among other properties and they need to be compatible with the substances in direct contact with them, for example, fuels [1]. Some robust materials widely used on automotive applications are Polyphenylene Sulfide (PPS), Polyphthalamide (PPA) and Polyoxymethylene (POM). They are characterized for having good chemical and heat resistance and they are mainly used on applications where requirements are demanding [2].

With the introduction of new fuels designed to reduce the consumption of fossil fuels and the pollutants emitted to the atmosphere [3], different biofuels have been developed [4]. A type of biofuel is biodiesel. Biodiesel is a fuel derived from vegetable oil or animal fats which is employed in diesel engines [4]. It is a mono-alkyl ester produced by trans esterifying the oil or fat with an alcohol [5]. Unlike other biofuels, biodiesel can be used with little or no modifications to engines [6]. One of the most common biodiesel fuels is the Soy Methyl Ester (SME) biodiesel. Despite of the advantages that biodiesel use can offer, it is more prone to cause material degradation than diesel, due to it is more oxidative nature [7], and thus, a compatibility study with the materials in direct contact with it is mandatory.

The present study aims to determine the effects of diesel and biodiesel on the mechanical properties of some of POM, PPA and PPS polymers, as well to assess if there is a significant difference among the diesel and biodiesel (BSM30A) effects over those grades.

Methodology

Materials

Five fuel resistant polymers commonly used on automotive industry were selected to assess the difference on the effects of diesel and biodiesel over the material mechanical properties. The chosen grades are shown in Table 1. These materials can be found on automotive components in direct contact with fuel, such as the fuel pump or other fuel-related systems.

Fuels

Diesel 2, a common grade used in North America and Biodiesel BSME30A, a volume mixture of 30% of aggressive Soy Methyl Ester and Diesel were selected for the study and prepared according to SAE J1681 [8].

Tests

In order to assess the effects of diesel and biodiesel on the polymer samples, compatibility tests were carried out. The experiment consisted on soaking the different polymer grades in the selected fuel during a period of 1008 hours at high temperature (120°C), simulating an extreme case of fuel exposure inside an automotive system.

Polymer tensile bars, with dumbbell shape, according to ASTM D638 [9] and ISO 527-2 [10], were employed to run the tests (Figure 1). Samples of each polymer grade were placed inside special containers designed to resist fuel compatibility tests. The containers were filled with either diesel or biodiesel, sealed and introduced into a hot chamber. Sampling was carried out at 168, 360, 504 and 1008 hours. Mechanical properties of the specimens were tested using an Instron 5581 machine (Figure 1), with a strain rate of 5 mm per minute [11].

Fourier Transform infrared spectroscopy was used to analyze the samples before and after the tests with the purpose of observe if there were changes on the polymer after the fuel exposure The instrument employed was a FTIR Nicolet iS10, Smart iTR from Thermo Scientific, with a 4 cm-1 resolution in the wavenumber range of 4000-500 cm^{-1}.

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Code	Family	Filler	Characteristics
PPS	Polyphenylene sulfide	40% glass reinforced	Strong and tough. Excellent heat and chemical resistance. Flame retardant.
PPA 1	Polyphthalamide, High performance polyamide	Unreinforced	Toughened and heat stabilized
PPA 2	Polyphthalamide, High performance polyamide	35% glass reinforced	Toughened and heat stabilized
POM 1	Polyoxymethylene	Unreinforced	Resistant to sour hot diesel
POM 2	Polyoxymethylene	25% Glass fiber	Resistant to fuel, specially oxygenated fuels

Table 1: Polymer grades selected for the tests.

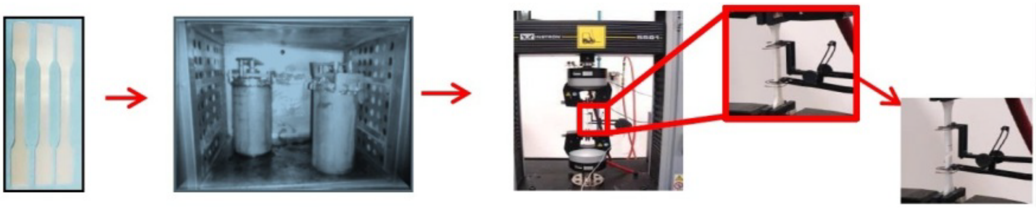

Figure 1: Experimental procedure.

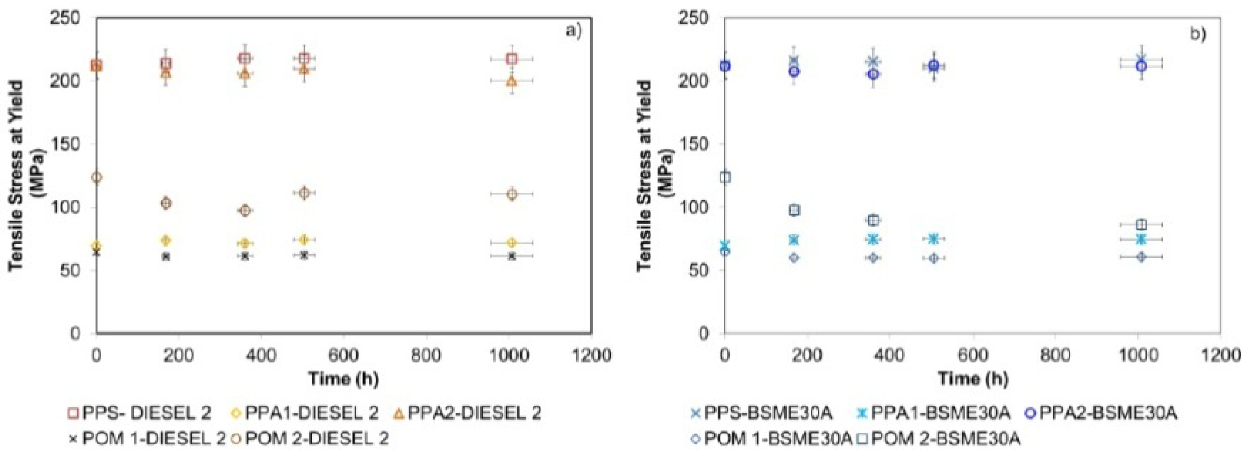

Figure 2: Tensile stress at yield for samples exposed to: a) Diesel 2, b) BSME30A.

Results and Discussion

Mechanical properties

Mechanical properties of each grade were evaluated for both fuel exposures. Figure 2 shows the tensile stress at yield variation after fuel exposure time. Tensile stress at yield was defined as the ultimate tensile stress point, in other words, it is the highest (smoothed) stress value after the yield point. As can be seen, yield strength does not show significant change for the different polymers exposed to diesel or biodiesel, with exception of POM 2-glass reinforced POM - , where the tensile stress at yield suffered a slight decrease. The PPS and the PPA 2- the one glass reinforced-obtained similar values for the tensile stress at yield in both fuels, while PPA1, POM 1 and POM 2 got lower values. The same trend was observed for tensile stress at break where, once again the fiber glass filled POM (POM 2) property suffered a decrease, perhaps because of the interfase POM polymer-Glass filler (Figure 3), which in combination with the lower chemical resistance of POM compared with PPA and PPS, it was more affected than the other samples.

Regarding the tensile strain at yield, it can be noticed in Figure 4 that for almost all the tested grades it diminished with fuel exposure for both diesel and biodiesel, with the exception of POM 1, which suffered a significant increase on this property (100%). The main change took place during the first 200 hours of exposure, varying just slightly after that. Again, both fuels had approximately the same effect over the samples. In this occasion, POM 1 had the highest tensile strain at yield, which means that got the highest elongation just before changing from elastic to plastic state. This was an unloaded polymer, which makes it more elastic than the loaded grades. It had the most accentuated change of the material grades analyzed. The less deformed grade was the PPS polymer, which suffer just slight variations on this property. PPA 2 and POM 2 obtained results closed to the PPS, due to the content of filler included on their formulas.

The behavior of the tensile strain at break is shown in Figure 5. Minimal changes are seen on PPS, POM 2 and PPA 2, when exposed to either diesel or biodiesel, while for PPA 1 and POM 1, this property decreased 50% of the original value when exposed to diesel 2 or BSME30A.

PPA 1 and POM 1 Young's Modulus were almost not affected by diesel and biodiesel (Figure 6). This means that the slope stress-strain did not change or, in other words, the deformation resistance for this material was not modified. The same property but for PPA 2 and POM 2, both materials with glass fiber filler, were increased slightly as well

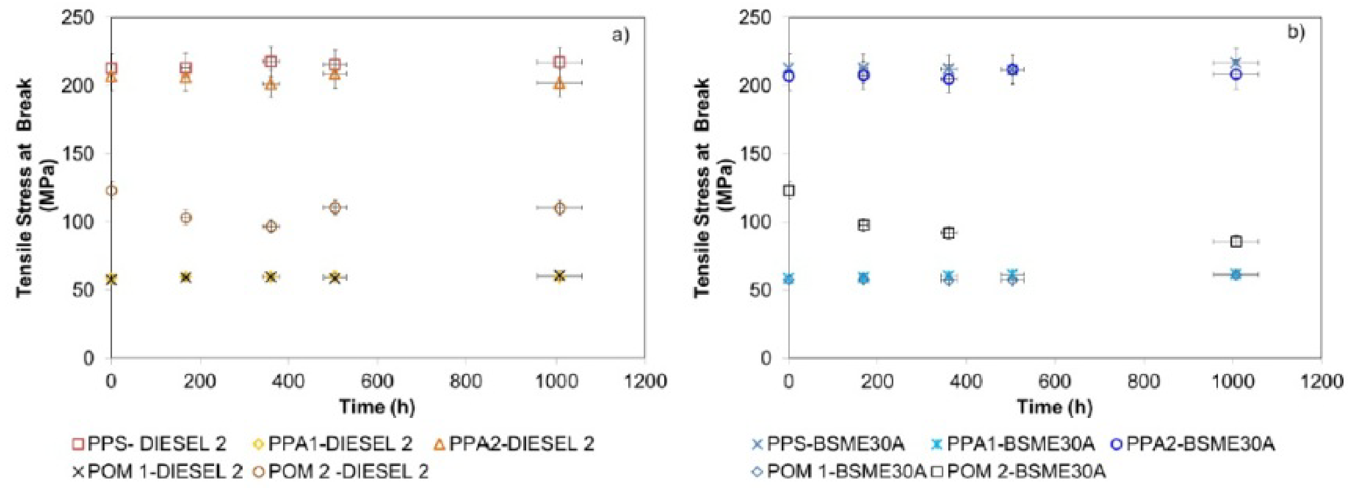

Figure 3: Tensile Stress at Break for samples exposed to: a) Diesel 2; b) BSME30A.

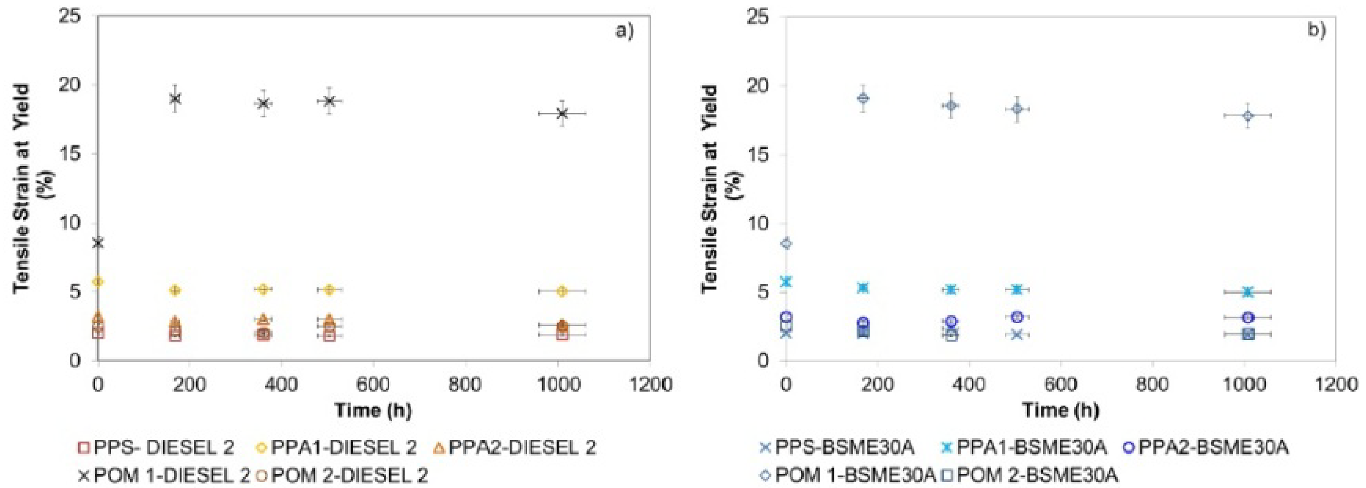

Figure 4: Tensile strain at yield for materials exposed to: a) Diesel 2; b) BSME30A.

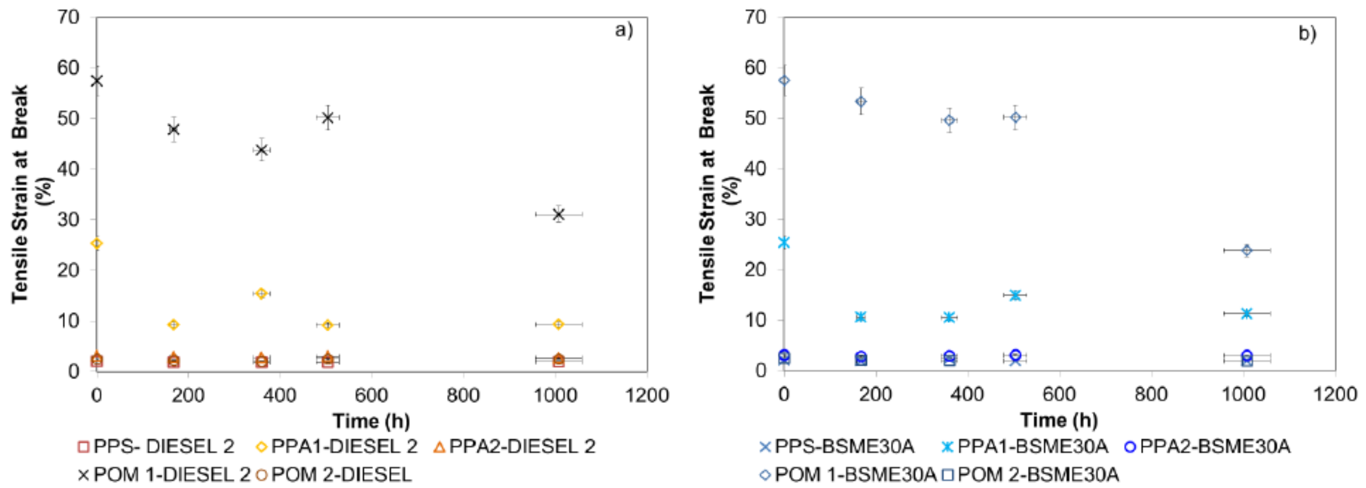

Figure 5: Tensile strain at break for materials exposed to: a) Diesel 2; b) BSME30A.

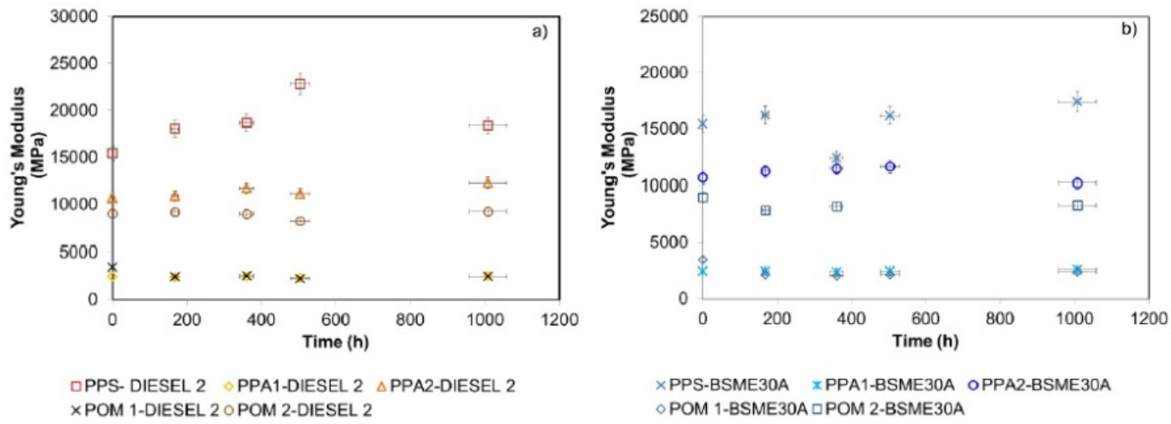

Figure 6: Young's Modulus for samples exposed to: a) Diesel 2; b) BSME30A.

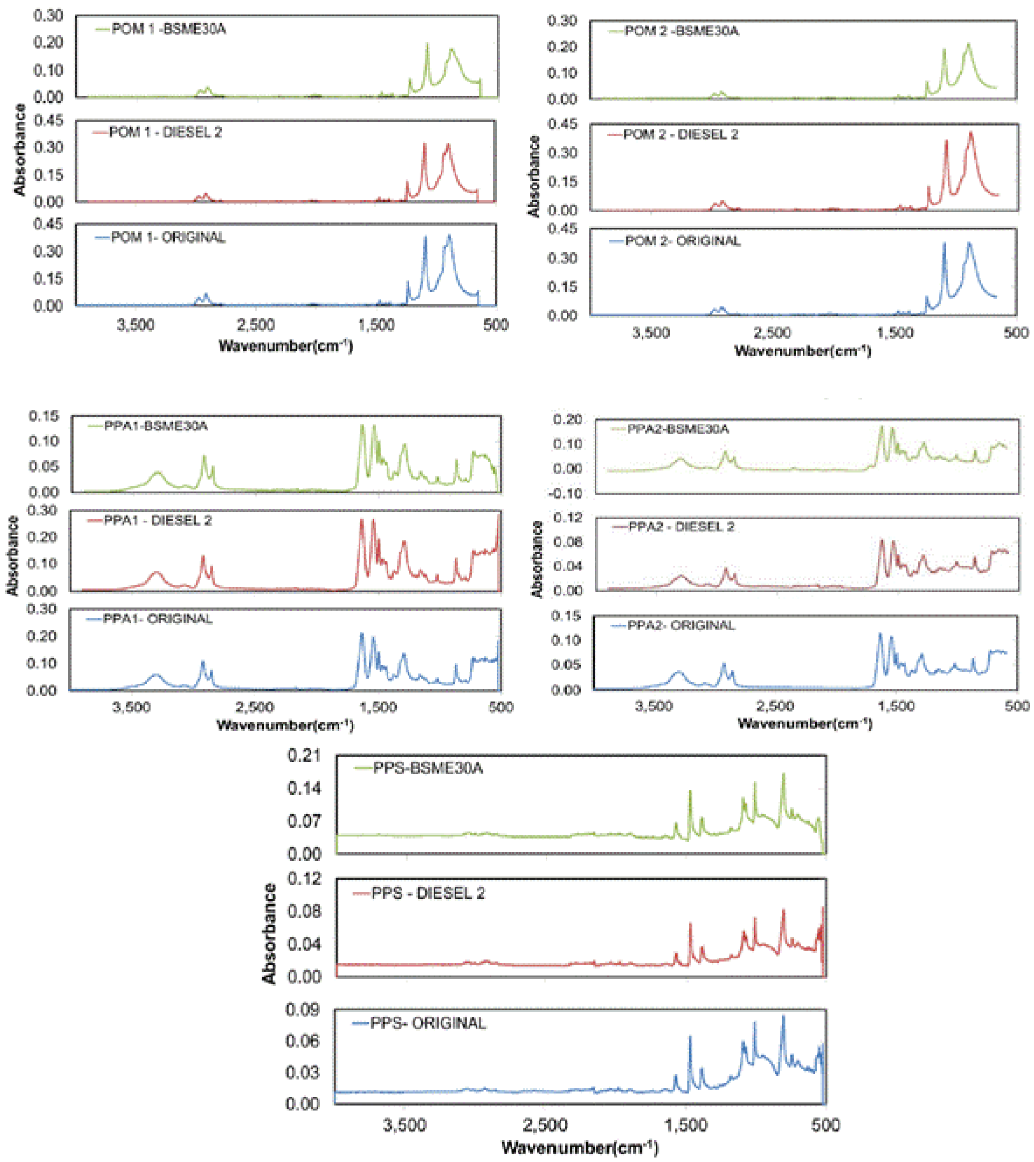

Figure 7: FTIR diagrams.

as for PPS. An increase on Young's Modulus can be interpreted as an augment of the material stiffness.

FTIR

FTIR analyses were carried out to check if there were observable changes on the polymers that were exposed to the fuel. Figure 7 shows the FTIR diagrams for the analyzed samples. OMNIC database was employed for interpretation [12].

Two adsorption bands can be observed in POM 1 and POM 2 diagrams: one strong band from 500 to 1500 cm^{-1} and one moderate from 2760 to 3020 cm^{-1}. The first one corresponds to the C-O stretching while the second one is due to the aliphatic hydrocarbons CH_{3-} and $-CH_{2-}$. These regions are in agreement with the zones reported by Baena et al. [13]. Only a slight difference was found for the POM 1 exposed to BSM30A for the band between 1050 and 940 cm^{-1}. The curve changes its shape, which means that the fuel originated a small change in the polymer structure, as small as it cannot be well detected by FTIR.

Regarding to the PPA polymers, the diagrams showed two adsorption bands: the first one from 500 to 1700 cm^{-1}, and the second one from 2780 to 3560 cm^{-1}. These bands correspond to the C-H stretching of aliphatic hydrocarbons (1460 to 1380 cm^{-1} and 2850 to 2975 cm^{-1}) and the stretching of primary and secondary aliphatic amides NH and NH_2 (3350 to 3180 cm^{-1} and 1570- 1515 cm^{-1}). No significant differences were found among the diagrams of PPA 1 exposed to diesel or biodiesel and the diagrams of original samples. A small new peak was observed for PPA 1 exposed to biodiesel from1600 to 1700 cm^{-1}, possibly because the fuel degraded slightly the polymer.

PPS diagram present one strong absorption region from 500 to 1600 cm^{-1} and a moderate band from 2800 to 3100 cm-1. These absorption bands correspond to vinyl olefins, and olefins, a double bond between adjacent carbon atoms C=C. Aliphatic Hydrocarbons are present too, with CH3 and CH2 vibrations. When curves from exposed to fuel and unexposed samples are compared only a small difference is observed at the band from 690 a 580 cm-1for the material exposed to biodiesel.

Conclusions

Diesel 2 and Biodiesel BSME30A have similar effects on the analyzed polymers (PPS, PPA1, PPA2, POM 1 and POM 2). Thus the substitution of Diesel 2 by Biodiesel BSME30A in applications were these polymers are employed do not cause a behavior different than the one produced by Diesel 2 concerning to the mechanical properties.

The diesel and biodiesel effects on the mechanical properties of the analyzed polymers were:

- The tensile stress at yield and the tensile stress at break were unaffected by the fuel exposure, with exception of the loaded POM, where these properties slightly decreased
- The tensile strain at yield diminished slightly for the tested grades with exception of the unloaded POM, in diesel and biodiesel, having the greatest changes during the first 200h of exposure. Loaded POM suffered an increase on this property
- The tensile strain at break was affected only in the PPA1 and POM 1 samples (the unreinforced specimens): it decreased more than 50% of its original value. This property remained almost constant for POM 2, PPA 2 and PPS polymers
- Young's Modulus remained unaltered for PPA 1 and POM 1, but it rose for PPA 2, POM 2 and PPS, the glass reinforced materials.

FTIR analyses showed only small differences among exposed and unexposed samples, mainly for the samples exposed to BSME30A.

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