INTRODUCTION

Biodiesel is derived from animal fats or vegetable oils and receiving much attention to partially or fully substitute the use of conventional petroleum diesel. With most of the properties being close to that of petroleum diesel, biodiesel provides some major advantages like higher cetane number, reduced exhaust emission, better lubricity, higher flash point, etc. [1-4]. The application of esters based on vegetable oils in premium quality diesel fuel ensures environmental advantages. Renewable fuels are expected to have a more and more considerable role in the future. Numerous researches has been carried out on different kinds of renewable fuels such as raw vegetable oil, waste cooking oil, biodiesels derived from various vegetable oils, etc. [5-8].

As the alternative fuel industry expands and matures, there is a need for research to prevent undesirable consequences in the field and to make the most of the potential benefits of alternate fuels. Degradation of polymers, used in fuel handling systems, is one of the topics relevant to the biodiesel compatibility issue. Concerns arise from the fact that biodiesel degrades through moisture absorption, oxidation, attack by microorganisms etc. during storage or use and thereby becoming more degradation. Oxidation of biodiesel reconverts esters into different mono-carboxylic acid such as formic acid, acetic acid, propionic acid, caproic acid, etc. which are responsible for enhanced degradation [9,10]. This process also increases free water content, which is undesirable because it may promote microbial growth and corrode fuel system components [11].

Availability of inadequate data on long term storage stability and transportation of biodiesel/its blends necessitate systematic laboratory studies under wide spectrum of experimental conditions to obtain more data on the compatibility between polymeric materials and biodiesel. Fuel stored for long periods can degrade, forming insoluble materials that will plug fuel filters on vehicles, foul engine injectors and form combustion system deposits that promote degradation. Fuel tankers, storage tanks, pipes and pumping equipment in an automobile are lined with different metals and polymers for failure-free operation of the automobile. Hence, the present investigation has been undertaken to study the effect of Pongamia biodiesel and their blends with commercial diesel at different temperature (25, 50 and 75 °C) exposed for different time intervals (120, 360 and 720 h) on two industrial important polymers namely polyphthalamide and polyarylamide that are used in automotive fuel systems. The results obtained are expected to help in understanding the degradation of mechanical properties like change in mass, change in volume,
tensile strength and hardness of PPA and PAA under various conditions of *Pongamia* biodiesel.

**EXPERIMENTAL**

Out of the most commonly used polymers, polyphthalamide (PPA) and polyarylamide (PAA) have been selected in the present study, as sufficient data related to these materials on compatibility with biodiesels aren’t available. The polymer sheets of 3 mm thickness were machined by die cutting into coupons of an area of 15 cm² (20 mm × 75 mm). Holes were drilled near the edge of the coupons. The test coupons were created as per ASTM G184. The coupons were cleaned by washing with distilled water and wiping with ethanol. The coupons were then dried by storing in a desiccator for further experimental studies. *Pongamia pinnata* biodiesel was collected from College of Agricultural Sciences, Bangalore, India. The characterization of *Pongamia pinnata* biodiesel (PPB) was performed as per ASTM D6751 in a testing laboratory.

**Static immersion test:** Coupons were weighed and fully immersed in 200 mL of test solution for a period of 120, 360 and 720 h at 25, 50 and 75 °C in triplicate. Different sets of experiments were carried for each parameter. Experiments were performed in triplicates. Averages of the determined data were analyzed.

**Material degradation under flow condition:** Rotating cage is a promising and reliable method to simulate pipeline flow under laboratory conditions to study the degradation behaviour of eight test coupons simultaneously. The rotating cage is fabricated as per ASTM G184. The acrylic vessel was filled with 4 L of test solution (PPB). The polymer samples were held between two Teflon holders, which have been designed to hold eight coupons. Experiments were conducted for a period of 120 h at the rotation speed of 500 rpm. Degradation of the tested materials was calculated from the difference in mass, volume, tensile strength and hardness of the coupons.

**Change in mass:** The test coupons were weighed before and after the tests and percentage (%) change in mass was determined by using the formula:

\[
\text{Change in mass (\%)} = \left( \frac{\text{Final mass (g)} - \text{Initial mass (g)}}{\text{Initial mass (g)}} \right) \times 100
\]

Positive values from the above formula indicate increase in mass and vice-versa.

**Change in volume:** Initial and final volume of the test coupons were found out by measuring the length, width and thickness of the test coupons using a vernier caliper before and after the tests. Then, percentage change in the volume was determined by using the formula:

\[
\text{Change in volume (\%)} = \left( \frac{\text{Final volume (g)} - \text{Initial volume (g)}}{\text{Initial volume (g)}} \right) \times 100
\]

Positive values from the above formula indicate increase in volume and vice-versa.

**Measurement of ultimate tensile strength (UTS):** Tensile strength of test coupons was performed before and after the experiment, using the universal testing machine (UTM) of 5 KN capacities. The tests were carried out to estimate the magnitude of the mechanical properties change of the material exposed to different conditions of biodiesel and their blends. The tests were performed as per ASTM D-638-03.

\[
\text{Decrease in UTS} = \left( \frac{\text{Original UTS} - \text{Final UTS}}{\text{Original UTS}} \right) \times 100
\]

**Measurement of hardness:** Hardness of test coupons was performed before and after the experiment, using the Rockwell Hardness Tester D Scale – 120° diamond spheroconical Indenter with 100 kgf load. The tests were carried out to estimate the change in hardness of the materials exposed to different conditions of biodiesel and their blends with diesel. The tests were performed as per ASTM-2240-75.

**Scanning electron microscopy:** Surface morphology of the samples after the exposure to different test media was characterized by scanning electron microscopy. The PPA and PAA polymer samples subjected to B100 at 25 °C for 720 h (static), 75 °C for 120 h (static) and 25 °C for 120 h (flow) conditions were characterized using scanning electron microscope (FEI NanoSEM 650).

**RESULTS AND DISCUSSION**

**Effect of temperature in mass change:** Fig. 1a and 1b shows the % change in mass of PPA and PAA test coupons exposed to different test media at different temperatures for 120 h. The % deviation in the mass was found to be in the range of 0.912 % (B100 at 25 °C) to 19.854 % (B0 at 75 °C) for PPA and 0.162 % (B0 at 25 °C) to 13.242 % (B100 at 75 °C) for PAA. As compared to room temperature, mass of PPA in pure biodiesel at 50 °C and 75 °C for 120 h are increased by 3.712 and 11.48 %, respectively and 1.939 and 13.242 %, respectively, at the rotation speed of 500 rpm.
respective for PAA. The major cause for the increased mass can be explained by the higher rate of diffusion of biodiesel in PPA and PAA at elevated temperatures [12].

**Effect of exposure time in change in mass:** Fig. 2a and 2b shows the % change in mass of PPA and PAA test coupons exposed to different test media at 25 °C for 120, 360 and 720 h. The deviation in mass was found to be in the range from 0.912 % (B100 at 120 h) to 3.59 % (B0 at 720 h) for PPA and 0.162 % (B0 at 120 h) to 1.51 % (B0 at 720 h) for PAA. Thus, it is evident from the observation that the effect of temperature on polymers is more than the effect of exposure time, because the % change in mass is more at elevated temperatures. As compared to 120 h, mass of PPA in pure biodiesel at 25 °C for 360 and 720 h are increased by 1.383 and 2.339 %, respectively and 0.386 % and 1.515 %, respectively for PAA. On the other hand, mass of PAA in pure diesel (B0) and their lower blends with biodiesel (B10 and B20) for 120 h and 360 h remains almost constant. From this, it can be inferred that PAA is more compatible in diesel and its lower blends with biodiesel (B10 and B20) than in pure biodiesel.

**Effect of exposure time in change in volume:** It is seen that the swelling of PPA and PAA exposed to different test media at 75 °C for 120 h. It can be observed that volume of PAA increased with factors like tensile strength and hardness, it is important to consider that for common elastomers, carbon black and silica fillers can serve to improve the hardness, abrasion resistance, tensile properties and tear strength. The addition of curing agents and accelerators cause cross-linking between the polymer chains or backbone and they also determine the physical properties. Upon exposure of different polymers into biodiesel, these cross-linking agent and/or filler seem to react with different components of biodiesel and thereby deteriorate the mechanical properties. In addition, hygroscopic nature of biodiesel may introduce water into polymer matrix. Diffusion of water into polymer matrix can also deteriorate the mechanical properties [12].

**Change in volume:** Fig. 3 shows the % change in volume of PPA and PAA exposed to different test media at 75 °C for 120 h. It can be observed that volume of PAA increased with biodiesel (B10 and B20) for 120 h and 360 h remains almost constant. From this, it can be inferred that PAA is more compatible in diesel and its lower blends with biodiesel (B10 and B20) than in pure biodiesel.

**Tensile strength:** The decrease in ultimate tensile strength, as represented in Fig. 4, ranged from 8-25 % for PPA and 10-18 % for PAA. The impact of 100 % biodiesel for 120 h at a temperature of 75 °C was the most significant for both PPA and PAA test coupons. Also, PAA showed lower % decrease in tensile strength than PPA (only 17.15 % for PAA vs. 24.54 % for PPA).

In order to understand the effect of biodiesel on mechanical properties like tensile strength and hardness, it is important to consider that for common elastomers, carbon black and silica fillers can serve to improve the hardness, abrasion resistance, tensile properties and tear strength. The addition of curing agents and accelerators cause cross-linking between the polymer chains or backbone and they also determine the physical properties. Upon exposure of different polymers into biodiesel, these cross-linking agent and/or filler seem to react with different components of biodiesel and thereby deteriorate the mechanical properties. In addition, hygroscopic nature of biodiesel may introduce water into polymer matrix. Diffusion of water into polymer matrix can also deteriorate the mechanical properties [12].

![Change in volume of PPA and PAA after immersion in test media at 75 °C for 120 h](image-url)
Hardness: Table 1 represents the hardness of as-received PPA and hardness after the immersion at different conditions. No change in hardness was observed at 25 °C for 120 h and 720 h, while a significant drop in hardness was observed for the PAA test coupons exposed to B100 at 75 °C for 120 h. For common polymers, carbon black and silica fillers can serve to improve the hardness, abrasion resistance, tensile properties and tear strength. The addition of curing agents and accelerators cause cross-linking between the polymer chains or backbone. It is this network of cross-links that largely determines these physical properties. Upon exposure of different polymers into biodiesel, these cross linking agent and filler seem to react with different components of biodiesel and thereby deteriorate the physical and mechanical properties [16].

<table>
<thead>
<tr>
<th>Media</th>
<th>Hardness before immersion</th>
<th>Hardness after immersion</th>
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<tbody>
<tr>
<td></td>
<td>25 °C, 120 h</td>
<td>25 °C, 720 h</td>
</tr>
<tr>
<td>B0</td>
<td>68-70</td>
<td>68-70</td>
</tr>
<tr>
<td>B100</td>
<td>68-70</td>
<td>67-69</td>
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</tbody>
</table>

Surface morphology of PPA and PAA: The SEM micrographs of untreated PPA, PAA and coupons exposed to B100 at 25 °C for 720 h and at 75 °C for 120 h are presented in Figs. 5 and 6, respectively. Non-uniformity of untreated coupons (Fig. 5a) was observed, which may be due to the manufacturing defects. Sample exposed to B100 at 25 °C for 720 h (Fig. 5b) exhibits occasional pits on the surface. Inflammation occurred on the surface coupons exposed to B100 at 75 °C for 120 h (Fig. 5c). These changes on exposed coupons confirm swelling, deformation and breaking of the polymeric material as a result of solvent action by the fuel mixture. Degradation process starts...
with the attack and penetration by the solvent beginning to create ampoules and then the formation and expansion of pits and removal of the base material along its surface.

Untreated PAA surface was found to be clean and uniform except a few irregularities, which may be due to the manufacturing defects (Fig. 6a).

Not much change in the surface of coupon exposed to B100 at 25 °C for 720 h except occasional pitting (Fig. 6b). More pits and inflammation have been found on the surface of the coupon exposed to B100 at 75 °C for 120 h (Fig. 6c), which may be due to increase in temperature. Material degradation and fuel properties depend on temperature. Higher temperature may aggravate the degradation and change in fuel properties at different level. Increase in temperature in fuel mixtures lead to an increased degradation behaviour.

**Material degradation under flow conditions:** The degradation behaviour for the studied polymers under flow condition (500 rpm) for 120 h in PPB as determined by evaluating change in mass and volume using rotating cage are presented in Fig. 7.

The values of mean change in mass of the PPA and PAA test coupons indicate the increase in mass after exposure to B100. Thus, PPA and PAA exhibit swelling behaviour when exposed to pure biodiesel. On the other hand, PAA with higher volume changes might not be the best fit for handling *Pongamia* biodiesel under flow conditions.

Table 3 represents the ultimate tensile strength of PPA and PAA before and after the exposure to pure biodiesel at room temperature. The % decrease in tensile strength of PPA was recorded to be 13.90 % while that of PAA was recorded to be 51.01 %. Clearly, PPA showed more resistance and durability under the flow conditions.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Before immersion</th>
<th>After immersion</th>
<th>Decrease in ultimate tensile strength (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPA</td>
<td>28.032</td>
<td>24.133</td>
<td>13.90</td>
</tr>
<tr>
<td>PAA</td>
<td>35.001</td>
<td>17.146</td>
<td>51.01</td>
</tr>
</tbody>
</table>

The change in hardness of PPA and PAA test coupons after exposure to flow conditions are represented in Table 4. It is observed that the decrease in hardness is more in PAA than in PPA.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Before immersion</th>
<th>After immersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPA</td>
<td>68-70</td>
<td>67-69</td>
</tr>
<tr>
<td>PAA</td>
<td>75-77</td>
<td>73-75</td>
</tr>
</tbody>
</table>

SEM micrographs of untreated PAA and PAA coupons and coupons exposed to B100 at 25 °C for 120 h under flow condition (500 rpm) are presented in Fig. 8.

Surface morphologies of PAA sample experienced a high level of deterioration and degradation compared to untreated ones, which is due to the presence of relative motion between the material and the biodiesel [17,18]. Scaling effect on the PAA surface (Fig. 8b) and formation of occasional pits on PPA surface (Fig. 8d) were observed after the exposure to flow condition.

On comparison of various mechanical properties, the order of usability of selected polymers was found to be PAA > PPA under static condition while PPA > PAA under flow condition.
The polymer backbone. There is a general rule describing the fact that polar substances are more likely to dissolve in polar solvents and non-polar substances are more likely to dissolve in non-polar solvents. It is noted that the polarity of PPA is less than that of PAA. Hence, the percentage gain in mass and volume of PPA decreases with the increasing concentration of biodiesel.

Conclusions

The major inferences drawn from the studies are as follows:

- The percentage gain in mass and volume of polymer samples increase with increasing concentration of biodiesel. Such changes can be attributed by the increased cross links in the polymer backbone. There is a general rule describing the fact that polar substances are more likely to dissolve in polar solvents and non-polar substances are more likely to dissolve in non-polar solvents. It is noted that the polarity of PPA is less than that of PAA. Hence, the percentage gain in mass and volume of PPA decreases with the increasing concentration of biodiesel.

- Upon the exposure to biodiesel, both tensile and hardness were greatly reduced for PPA and PAA materials as compared to that in as-received condition.

- The scanning electron microscopy of the treated test coupons of PPA and PAA showed significant changes in surface morphology as compared to that of as-received condition. Degradation was more in flow conditions than in static condition due to the presence of relative motion between the material and the biodiesel.

- The overall sequence of compatible polymers in PPB under static condition was found to be PAA > PPA. According to this comparison, PAA was found to be the best material to use in fuel storage tanks.

- Similarly, the overall sequence of compatible polymers in PPB under flow condition was found to be PPA > PAA. Thus, PPA can be used in the fuel transmission pipe lines for their longer life.

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REFERENCES