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A Study of Polystyrene Solubility in Biodiesel

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http://dx.doi.org/10.5772/59112

1. Introduction

Waste plastics, such as polystyrene (PS), polypropylene (PP), and polyethylene (PE), are usually disposed together and so require time for sorting. Polystyrene articles (e.g., Styrofoam, food trays, and packing materials) occupy a large volume at a very low weight. This results in inefficient transportation of waste plastic. In addition, subjecting waste plastics to pyrolysis, which involves conversion of plastic to oil requires energy and is expensive. It would be useful to reduce waste plastic volume and to recover the energy of waste polystyrene recycling by a simple process. In this chapter, a simple process is proposed to obtain liquid fuel dissolved polystyrene in biodiesel at lower energy costs.

As shown in Figure 1, waste polystyrene such as expanded polystyrene is selectively dissolved in biodiesel derived from waste cooking oil, and biodiesel-dissolved polystyrene is utilized as diesel fuel for a cogeneration system. This chapter describes the potential for selective dissolution of polystyrene in biodiesel, which consists of fatty acid methyl esters (FAME), by using Hansen solubility parameters and for properties and combustion characteristics as diesel fuel by using fuel ignition analyzer.

The results obtained by Hansen solubility parameters indicated that methyl oleate, the main component of biodiesel, provides selective solubility for polystyrene. Results of experiments that examined solubility properties revealed that the kinematic viscosity increased with polystyrene concentration in FAME derived from soybean cooking oil. The cause of the increase in kinematic viscosity was due to the presence of a polymer with a molecular weight of up to approximately $10^7$.

On examining the use of dissolved polystyrene as fuel for diesel engines, experiments showed that the cetane number decreased with an increase in polystyrene concentration; however, the cycle-to-cycle fluctuations in combustion pressure and ignition timing when polystyrene dissolved in FAME was used were less than those found for neat FAME. Polystyrene dissolved
in FAME crystallized and precipitated in the gel upon addition of hydrocarbons such as engine lubricant oil. Therefore, the use of FAME-dissolved polystyrene as diesel fuel requires attention to tribology.

**Figure 1.** Energy recovery using biodiesel fuel (FAME) derived from waste cooking oil selective-dissolved waste poly-styrene (PS).

Biodiesel consists of fatty acid methyl esters (FAME) and can be produced from a great variety of feedstocks including vegetable oil (e.g., soybean, palm, rapeseed oil) and animal fats, as well as waste cooking oils (e.g., used frying oils). FAME has been used as alternative fuel of diesel fuel. Many research projects have been carried out and have been published in books and journals [1-3]. Most of all are concerning to fuel quality, combustion and exhaust emission characteristics, which regards the utilization with the diesel engines.

Effective use of waste plastics is important in establishing a recycling-oriented society. FAME can dissolve plastics and rubbers, which are used as fuel system parts of diesel engines, resulting in the need to replace these parts. If a method to utilize FAME as a solvent to dissolve plastics can be developed, waste plastics could be recovered and could be utilized as liquid fuel.

Several studies on solubility report that \( n \)-alkenes and di-\( n \)-alkyl are better solvents for the low and medium molecular weight samples of polystyrene than the corresponding \( n \)-alkanes [4]. Also, it is shown that certain food items have been shown to be incompatible with the expanded polystyrene (EPS) used for the manufacture of food containers. Citronella, limonene and terpinene, which are constituents of many flavor oils, are excellent solvents for polystyrene [5].

Studies of solubility for volume reduction and waste management of polystyrene recycling have been conducted earlier [6,7]. Solubility values of extrude poly-styrene(XPS) in several solvents such as benzene, toluene, xylene, tetrahydrofuran, chloroform, 1,3-butanediol, 2-butanol, linalool, geranoil, \( d \)-limonene, \( p \)-cymene, terpinene, phellandrene, terpineol, metha-
nol, eucalyptus, cinnamaldehyde, nitrobenzene, N,N-dimethylformamide, and water have been determined. The solubility of the polymer in the mentioned solvents at different temperatures has been investigated. The solvent can be easily recycled by distillation.

Polystyrene dissolved in FAME has a greater heating value as fuel than that of FAME alone, so that a reduction of the fuel consumption per output and the increase in the use of diesel and boiler cogeneration can be expected. The diesel combustion characteristics of soybean oil FAME-dissolved packing peanuts has been investigated by Kuzhiyil et al. [8]. The results showed that engine power increased initially with the polystyrene concentration and then decreased at concentrations greater than 5%. The decline in engine power at high polystyrene concentrations could be caused by the poor spray atomization and deteriorated combustion efficiency due to the high viscosity of polystyrene mixtures.

Studies on the use of soy methyl ester-polystyrene (SME-PS) blends to increase durability of concrete have been conducted [9,10]. Experimental results show that SME-PS reduces water absorption of concrete (by up to 75%), protects from damage caused by freezing and thawing (reduces damage by 66%), reduces chloride ingress depth by up to 50%, and slows the rate of the alkali-silica reaction by 50%.

The method for solubilizing polystyrene in a fatty acid ester has been granted as a US patent [11]. The purpose of the invention is to produce commodity material useful for the production of polymers from polystyrene dissolved in fatty acid esters. This patent also provides the method for disposing of polystyrene solubilized in a fatty acid ester. A fatty acid ester composed of a variety of alkyl and alkene esters is used and heated to temperatures between 100°C and 180°C.

Expanded polystyrene (EPS) is used for packaging material to cushion appliances and containers of seafood and agricultural products. Extruded polystyrene (XPS) board is used as insulating material in building. The production of EPS in the world came up to 10 Mt in 2010. Presently, various EPS organizations from more than 25 countries around the world have subscribed to the international agreement on recycling of EPS. In Japan, EPS of 1.1 Mt was produced and 88% of waste EPS was recovered by means of material recycling and energy recovery in 2010; however, the EPS trays with food residue were not recovered. Almost all were sent to landfill sites or were incinerated. EPS and XPS are low density, high volume materials, which consume a significant amount of space in a landfill. The transport efficiency of waste polystyrene is poor because its volume-to-mass ratio is large. Reducing the volume of waste EPS and XPS will reduce CO₂ emissions and decrease the cost of energy per volume due to the transportation of waste plastic.

2. Experimental

2.1. Solubility parameter determination

Solubility parameters can be used to easily identify solvents for polymers. Many successful studies have used methods based on the solubility parameter [12-14]. The term "solubility
parameter” was first used by Hildebrand and Scott [15]. The theory relates the energy of mixing to the energy of vaporization of the pure component. This theory was developed for mixing of nonpolar substances. However, many solvents and polymers in common use are polar compounds. Hansen divided the polar portion into a dipole-dipole contribution and hydrogen-bonding contribution, both of which could be determined through solubility experiments with polymers [16]. The Hansen solubility parameter (HSP) separates the solubility energy into three parts: dispersion (δ_D), polarity (δ_P), and hydrogen bonding (δ_H). The HSP concept can be described as “like vectors dissolve like vectors.” For the vector “likeness,” the HSP distance (Ra), which is the distance between the solvent and center of the polymer solubility sphere, was used. Ra is calculated using Eq.1:

\[
R_a = \sqrt{4(d_{D1} - d_{D2})^2 + (d_{P1} - d_{P2})^2 + (d_{H1} - d_{H2})^2}
\]

(1)

where subscript 1 represents the solvent, and subscript 2 represents the polymer.

This equation was developed from plots of experimental data where the constant “4” was found convenient and correctly represented the solubility data as a sphere encompassing the good solvents. When the scale for dispersion (δ_D) parameter is doubled, in comparison with other two parameters essentially spherical, rather than spheroidal, regions of solubility are found [16].

To determine if the parameters for the solvent and polymer are within an acceptable range, a value called the interaction radius (R_0) of the polymer is applied to the substance being dissolved. Good solvents are within R_0, and poor ones are outside it. A simple composite affinity parameter, relative energy distance (RED), has been defined as:

\[
RED = R_a / R_0
\]

(2)

Good solvents will have RED less than 1.0. Poor solvents will have increasingly higher RED values.

In this study, the solubility of polymer in methyl ester, methanol, and fatty acid was determined by HSPiP (Hansen solubility parameters in practice) software [17]. Fatty acids are source materials of FAME production by esterification process. Oleic acid methyl ester (methyl oleate) is a main component of FAME derived from waste cooking oil, because a typical raw material for cooking oil is the rapeseed oil and soybean oil. Tables 1 and 2 show the HSP from the dataset in HSPiP for methyl oleate, methanol, and oleic acid as solvents, and polystyrene (PS), polypropylene (PP), and polyethylene (PE) as polymers. The HSP generally in use for liquids have all been calculated at 25°C. In this study, the dataset at 25°C was used.
Table 1. Dispersion $\delta_D$, polarity $\delta_P$, and hydrogen bonding $\delta_H$ of methyl oleate, methanol, and oleic acid as solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dispersion $\delta_D$ (MPa$^{1/2}$)</th>
<th>Polarity $\delta_P$ (MPa$^{1/2}$)</th>
<th>Hydrogen bonding $\delta_H$ (MPa$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Oleate</td>
<td>16.2</td>
<td>3.8</td>
<td>4.5</td>
</tr>
<tr>
<td>Oleic Acid</td>
<td>16</td>
<td>2.8</td>
<td>6.2</td>
</tr>
<tr>
<td>Methanol</td>
<td>14.7</td>
<td>12.3</td>
<td>22.3</td>
</tr>
</tbody>
</table>

* data from the dataset in HSPiP [17]

Table 2. Dispersion $\delta_D$, polarity $\delta_P$, and hydrogen bonding $\delta_H$ and interaction radius of polystyrene (PS), polypropylene (PP), and polyethylene (PE) as polymer.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Dispersion $\delta_D$ (MPa$^{1/2}$)</th>
<th>Polarity $\delta_P$ (MPa$^{1/2}$)</th>
<th>Hydrogen bonding $\delta_H$ (MPa$^{1/2}$)</th>
<th>Interaction radius $R_0$ (MPa$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>18.5</td>
<td>4.5</td>
<td>2.9</td>
<td>5.3</td>
</tr>
<tr>
<td>PE</td>
<td>16</td>
<td>0.8</td>
<td>2.8</td>
<td>3.2</td>
</tr>
<tr>
<td>PP</td>
<td>18</td>
<td>0</td>
<td>1</td>
<td>6</td>
</tr>
</tbody>
</table>

* data from the dataset in HSPiP [17]

2.2. Measurement of the solubility and fuel properties

Expanded polystyrene (EPS) and food trays (PSP), cut to pieces, were stirred slowly into FAME and dissolved at room temperature. FAME was prepared by the batch-type production equipment using an alkaline catalyst method [3]. Commercial soybean cooking oil was used as the raw material to produce biodiesel, soybean oil methylester (SME).

To determine the dissolved molecular weight of the polystyrene, polystyrene standards with an average molecular weight (MW) of 4000 and 50,000 were also dissolved in FAME. The polystyrene molecular weight distribution in FAME was measured by gel permeation chromatography (GPC).

To clarify the fuel characteristics as diesel fuel, kinematic viscosity was measured according to JIS K2283, the ignition quality as diesel fuel was analyzed by fuel ignition analyzer (FIA) through constant-volume combustion (Fueltech, FIA-100 ver3). Diesel combustion property was evaluated by an ignition delay. Figure 2 shows the configuration of the FIA. In the experiments, conducted under constant pressure of 2.0MPa and initial temperatures of 450°C, the fuel was injected and the ignition delay was measured. Ignition delay was defined as the time difference between the fuel injection start time and the time at which combustion pressure was 0.02MPa greater than the initial pressure in the chamber, as shown in Figure 3.

The cetane number (CN) is used often for estimating ignition quality. In this study, the CN value of FAME-dissolved polystyrene was estimated by calibration of the CN obtained from
a mixture hexadecane (CN=100) and heptamethylnonane (CN=15). For practical purposes, the FIA cetane number($CN_{FIA}$) was determined by Eq.3.

$$CN_{FIA} = \frac{1}{1413\cdot e^{-0.69\tau}}$$

(3)

where $\tau$ denotes the ignition delay [ms].

Furthermore, the relationship between $CN$ of FAME using FIA and $CN$ value using the CFR standard institutional organization engine test, $CN_{CFR}$ is described by the following relation [18]:

$$CN_{CFR} = CN_{FIA} + 22$$

(4)

One of the important characteristics of diesel fuel is the carbon residue (CR). The CR is a characteristic value related to the amount of carbon deposits stored inside the engine, carbon deposits for petroleum-based fuels in general are measured using a sample condensed to 10% in volume. For FAME, the high-temperature heating process under condensation results in thermal decomposition of FAME components. In addition, the chemical structure of the fatty acid methyl ester component is changed. For this reason, the CR value for FAME was measured using a sample without condensation in this study.

The heating value of fuel is related to fuel economy and engine power. In this study, the higher heating value of fuel was measured using an automatic bomb calorimeter (Shimadzu, CA-4PJ).

![Figure 2. Configuration of fuel ignition quality analyzer (FIA).](image)
3. Results and discussion

3.1. Solubility of polymers

Figure 4 represents data of the polymers as mesh spheres, and the solvents as dots. Figure 5 also represents the data as two-dimensional planes. Table 3 shows the results calculated from the HSP analysis. In Figures 4 and 5, the scale in coordinate of dispersion($\delta_D$) is expressed in HSPiP as twice as large as those in coordinates of polarity($\delta_P$) and hydrogen bonding($\delta_H$), due to the coefficient "4" of dispersion component in Eq.1.

In Figures 4 and 5, it seems that the methyl oleate is inside of polystyrene (PS) and polypropylene (PP) spheres, methanol and oleate acid are outside of them. From RED value in Table 3, the combination of PS and methyl oleate had a RED value less than 1.0. The PP and polyethylene (PE) combinations with methyl oleate had RED values slightly higher than 1.0. This indicates that methyl oleate is significantly outside the PE and PP spheres. The RED value of methanol and oleic acid are significantly greater than 1.0. Therefore, only polystyrene can be considered to be sufficiently dissolved in methyl oleate. The results also show that FAME will selectively dissolve the polystyrene in the form of mixed waste plastic.
3.2. Characteristics of FAME-dissolved polystyrene

To examine solubility, both the food trays (polystyrene paper; PSP) and the expanded polystyrene (EPS) were completely dissolved in FAME, which was completely transparent.
after the dissolution, as shown in Figure 6. Figure 7 shows the relation between kinematic viscosity and mass concentration of PS dissolved in FAME. The figure also shows results obtained by another researcher [8] and the dissolved polystyrene standards (average molecular weight of 4000 and 50,000). Kinematic viscosity increased with increasing PSP and EPS concentrations. For EPS, kinematic viscosity increased exponentially, revealing a high kinematic viscosity such as that of heavy oil at a concentration of 9%(m/m) EPS in FAME. In contrast, the kinematic viscosity of the PS standard in FAME was less than those of EPS and PSP. In addition, the kinematic viscosity increased with an increase in average molecular weight, suggesting that an increase in kinematic viscosity is related to the degree of polymerization and molecular weight of the dissolved polystyrene.

![Figure 6. Photos of FAME dissolved polystyrene.](image)

![Figure 7. Relationship between kinematic viscosity and mass concentration of the polystyrene dissolved in FAME.](image)
The molecular weight distribution of polystyrene in FAME was measured by GPC. Figure 8 shows the experimental results for the polystyrene (PS) standard with an average molecular weight of 50,000 dissolved in FAME and 5%(m/m) EPS in FAME. The molecular weight peak was similar to that of the polystyrene standard; however, the EPS molecular weights in FAME were distributed across a wide range compared to the range of the PS standard, and indicated a compound with a molecular weight greater than $10^7$. These results suggest that the existence of a very large polymer causes an increase in kinematic viscosity.

Next, the rate of volume reduction of polystyrene and PSP caused by dissolution in FAME was investigated. The solvent n-hexane—a non-polar solvent—was added to crystallize the PS. The crystallized PS was filtered and the mass was measured to determine specific volume. The specific volume of PS in FAME was $1.38 \times 10^{-3} \text{ m}^3/\text{kg}$, indicating that the specific volume of $82.6 \times 10^{-3} \text{ m}^3/\text{kg}$ for PS before dissolution was reduced. Therefore, dissolution of PSP in FAME can reduce the volume of waste plastic. Also, in case of EPS and XPS which show high expansion ratio, the volume will be extremely reduced by dissolution in FAME.

![Figure 8. Distribution of polystyrene molecular weight in FAME.](image)

### 3.3. Fuel characteristics

Figure 9 shows a series of combustion pressures obtained by the FIA fuel ignitability tester. The cycle-to-cycle fluctuation in combustion pressure for EPS dissolved in FAME is less than that for neat FAME.

Figure 10 shows the changes in ignition delay and cetane number ($CN_{FIA}$) against the dissolved EPS concentration. The ignition delay gradually increased with increasing EPS concentration. For this reason, the $CN_{FIA}$ value also decreases. This is caused by the increased kinematic viscosity and the suppression of fuel spray atomization upon dissolution of EPS. Furthermore, generally the petroleum-based fuels are known to possess poor ignitability at higher concentrations of aromatic hydrocarbons. The raw material for styrene monomers is represented by the aromatic chemical formula of $C_8H_8$. For this reason, the ignition delay gradually increases with PS concentration.
Figure 9. Courses of combustion pressure obtained by FIA fuel ignitability tester.

Figure 10. Changes of ignition delay and cetane number ($CN_{FIA}$) against the dissolved polystyrene (EPS) concentration.

Figure 11 shows the relation between calorific value and EPS concentration. Initially, the dissolution of EPS in FAME was expected to result in a sufficiently high heating value. However, the increase at a lower heating value was greater than that at the higher heating value, because the oxygen content in the original FAME of approximately 10%(m/m) is reduced by dissolution of EPS.

Figure 11. Effect of polystyrene (EPS) concentration in FAME on higher calorific value.
Table 4. Comparison of density, kinematic viscosity, higher heating value, cetane number (\(\text{CN}_{\text{FIA}}\)), and carbon residue without sample condensation.

<table>
<thead>
<tr>
<th>Properties</th>
<th>FAME(SME)</th>
<th>EPS-2%(m/m) in FAME(SME)</th>
<th>EPS-5%(m/m) in FAME(SME)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density kg/L@15°C</td>
<td>0.886</td>
<td>0.888</td>
<td>0.894</td>
</tr>
<tr>
<td>Kinematic viscosity mm(^2)/s@40°C</td>
<td>4.16</td>
<td>6.46</td>
<td>19.5</td>
</tr>
<tr>
<td>Higher heating value MJ/kg</td>
<td>39.6</td>
<td>40.8</td>
<td>39.8</td>
</tr>
<tr>
<td>Cetane Number (\text{CN}_{\text{FIA}})</td>
<td>28</td>
<td>27</td>
<td>23.5</td>
</tr>
<tr>
<td>100%-Carbon residue %(m/m)</td>
<td>0.012</td>
<td>0.042</td>
<td>0.078</td>
</tr>
</tbody>
</table>

Table 4 shows the density, kinematic viscosity, higher heating value, cetane number (\(\text{CN}_{\text{FIA}}\)), and carbon residue without sample condensation. The carbon residue at 5\%(m/m) dissolved EPS was twice that at 2\%(m/m) dissolved EPS. When this was used as diesel fuel, the amount of carbon deposit in the combustion chamber increased. This deposit may affect the fuel injection system and fuel spray atomization.

Figures 12 and 13 show the effect of fatty acid components of FAME on kinematic viscosity and carbon residue. As shown in Figure 12, the kinematic viscosity increases with an increase in concentration of EPS, and the fatty acid methyl ester with higher carbon number shows higher kinematic viscosity. Also, the carbon residue at methyl oleate shows higher value than methyl palmitate and methyl laurate at all concentrations of EPS. From the results, fuel properties of FAME dissolved EPS may be improved by changing fatty acid composition in FAME. In other words, to use FAME dissolve EPS as fuel, FAMEs with short and middle length of carbon chains as fatty acid component will be better than fatty acid methyl ester with the long length chains.

### 3.4. Diesel engine performance

This section describes the engine performance and problem of diesel generator fuelled with FAME dissolved EPS. The experiment was carried out by using small diesel engine generator. Fuel consumption was measured by a burette-installed fuel line at various engine loads. And the brake thermal efficiency was calculated. Table 5 shows the main specification of engine generator used in experiment. Figure 14 shows the result obtained by engine test. From Figure 14, the thermal efficiency at the FAME dissolved EPS-5\% shows higher value than that at neat FAME at rated engine output. This might be caused by lower cycle-to-cycle fluctuation in combustion as shown in Figure 9 in case of EPS-5\%.

In general, the lubricating oil in the diesel engine was mixed with some injected fuel, a process called “oil dilution by fuel.” Then, a mixing test that involved mixing of regular diesel lubricant hydrocarbons and FAME-dissolved EPS was conducted. Figure 15 shows the photos of
mixture with regular diesel lubricant hydrocarbon and with lubricant oil derived from castor oil. These photos show that, immediately after mixing, the dissolved EPS crystallizes in the gel and precipitates for both cases. Thus, the use of FAME- dissolved polystyrene as diesel fuel requires the prevention of precipitation and deposition of polystyrene.

### Diesel engine generator

<table>
<thead>
<tr>
<th>Type</th>
<th>Yanmar L40A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct-injection</td>
<td></td>
</tr>
<tr>
<td>Single cylinder</td>
<td></td>
</tr>
<tr>
<td>Air-cooled</td>
<td></td>
</tr>
<tr>
<td>Bore x Stroke</td>
<td>68 mm x 55 mm</td>
</tr>
<tr>
<td>Displacement</td>
<td>199 cm³</td>
</tr>
<tr>
<td>Compression ratio</td>
<td>20</td>
</tr>
<tr>
<td>Injection nozzle</td>
<td>YDLL-P type</td>
</tr>
<tr>
<td></td>
<td>4holes-0.22mm</td>
</tr>
<tr>
<td></td>
<td>150 degree of spray angle</td>
</tr>
<tr>
<td>Rated engine output</td>
<td>2.4kW/3,600rpm</td>
</tr>
</tbody>
</table>

**Table 5.** Main specification of diesel generator.

![Graph](image_url)

**Figure 12.** Effect of polystyrene (EPS) concentration in FAME on kinematic viscosity.
Figure 13. Effect of polystyrene (EPS) concentration in FAME on carbon residue.

Figure 14. Brake thermal efficiency vs. engine load of diesel engine generator.

Figure 15. Photo of mixture of FAME-dissolved EPS and engine lubricant oil.
4. Conclusions

1. The potential for dissolution of polystyrene in fatty acid methyl esters (FAME) was estimated using Hansen solubility parameters. Results indicated that FAME provides selective solubility for polystyrene.

2. Results of experiments that examined solubility properties revealed that the kinematic viscosity increased with polystyrene (EPS) concentration in FAME. The cause of the increase in kinematic viscosity was due to the presence of a polymer with a molecular weight of up to approximately $10^7$.

3. The volume of polystyrene (PSP) can be reduced by approximately 1/60 by dissolution in FAME.

4. When examining the use of dissolved EPS as fuel for diesel engines, experiments showed that cetane number decreased with an increase in EPS concentration; however, the cycle-to-cycle fluctuation in combustion pressure and ignition timing when using EPS dissolved in FAME were less than those found for neat FAME.

5. EPS dissolved in FAME crystallized and precipitated in the gel upon addition of hydrocarbons such as engine lubricant oil. Therefore, the use of FAME-dissolved polystyrene as diesel fuel requires attention to tribology.

Acknowledgements

We would like to express our appreciation to Mr. Ryuta Onishi, graduate student from the University of Shiga Prefecture, for his assistance with the experiments.

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