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Biodiesel permeability in polyethylene

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Biodiesels
Diffusivity
Solubility
Permeability
Modelling

Abstract
This paper reports solubility and diffusivity data for soy and rapeseed methyl esters in polyethylene together with comparisons with methyl oleate and linoleate. These data showed that there is no significant difference in diffusivity and solubility between all these penetrants. Data were used to discuss the reliability of predictive models for diffusion and solubility of additive type molecules into semi-crystalline thermoplastic polymers. Permeability data were monitored by a new device, the results from which are in reasonable agreement with theoretical considerations on solubility and diffusivity. They also showed that biodiesels are less aggressive towards polyethylene than diesel from a petrochemical source.

1. Introduction

A recent trend in the automotive industry is to replace fossil fuels by fuels from vegetal sources. Methyl esters from vegetal sources are made of several kinds of saturated and unsaturated linear hydrocarbon chains [1]. There is a considerable literature dealing with their production, but there are only few data showing their good compatibility with the various polymers employed in the fuel system [2], which is necessary for their sustained use. In particular, little is known on interactions of fatty esters with polyethylene (PE in the following). Non-empirical lifetime assessment is possible if:

- The permeation kinetics of methyl esters in polymer can be predicted for a given temperature, sample thickness, sample crystalline ratio and biodiesel type,
- Structure-properties relationships are available to determine the effect of oil absorption on mechanical properties: Young’s modulus, yield stress, crazing critical strain, etc...

The aim of this article is to study the transport properties in PE of soy and rapeseed oils and answer the following questions:

- Are the biodiesels from vegetable source more aggressive towards PE than classical diesels derived from crude oil? Note that the answer to this question comes also from the relative oxidizability of matrix and penetrant: if the penetrant is much more oxidizable than polymer, one can imagine that absorbed penetrant may promote oxidative degradation of the matrix by a co-oxidation mechanism. This question is under investigation in our laboratory
- Despite the relative complexity of vegetable methyl ester composition, do model systems exist?
- Can permeation properties be modelled in order to build a predictive tool? Can the model take into account the morphological differences between all commercial grades of PE?

Methyl oleate (C18-1) and methyl linoleate (C18-2) being the major components of the vegetable oils [2], it seemed to us interesting to study their permeability independently and to compare their transport properties to those of vegetable methyl esters. This paper is also aimed at

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validating a new cell designed for measuring fluid permeability through polymers.

2. Experimental

2.1. Materials

2.1.1. Polyethylene

The polyethylene was a pipe grade supplied by Borealis as additive-free powder. This was blended with 0.3% (w/w) Irganox 1010 and then extruded using a Brabender twin-screw extruder to obtain 150 μm films using the following conditions (Tzone 1 = 150 °C, Tzone 2 = 180 °C, Tzone 3 = 200 °C), torque = 400 N m, rev = 10 tr min⁻¹.

Several PE extruded foils were then pressed together at 130 °C using a laboratory press (Brigite Instruments) in order to obtain 600 ± 100 μm films, this thickness being optimum for the diffusion experiments under study. The polymer density was about 0.935. Melting point was found to be close to 128 °C. Crystalline ratio was estimated to be close to 40% from measurement of melting enthalpy by differential scanning calorimetry using ΔH₁₀₀ = 290 J g⁻¹ for a 100% crystalline material.

Some comparisons were done with a commercial grade of HDPE (polyethylene 2 in the following) supplied as 0.2% carbon black filled tanks made by extrusion blowing. M_W was estimated to be close to 225 kg mol⁻¹ by dynamic rheometry. Crystalline ratio was estimated to be close to 60% from measurement of melting enthalpy.

2.1.2. Penetrants

Commercial methyl oleate (CAS 112-62-9, ref 268038 supplied by Sigma Aldrich) and methyl linoleate (CAS 112-63-0, ref 62290 supplied by Sigma Aldrich) were used for sorption experiments. Rapeseed and soy methyl esters were kindly supplied by Sofiproteol.

![Pictures of a liquid permeation cell.](image)

Fig. 1. Pictures of a liquid permeation cell.

![Kinetic curves for mass uptake of rapeseed methyl ester sorption into polyethylene 1 at 75 °C (a), 60 °C (b), 45 °C (c) and room temperature (d).](image)

Fig. 2. Kinetic curves for mass uptake of rapeseed methyl ester sorption into polyethylene 1 at 75 °C (a), 60 °C (b), 45 °C (c) and room temperature (d).
2.2. Characterization

2.2.1. Solubility and diffusivity measurements

5 cm x 2 cm samples were immersed in methyl esters at various temperatures from room temperature to 75 °C in ventilated ovens. Methyl esters were thermally equilibrated overnight prior to exposure. It was ensured that PE samples were totally immersed under a huge quantity of methyl ester, and that PE samples were not mechanically stressed by vessel walls. Each measurement was made in triplicate.

After exposure, immersed samples were quickly removed from the methyl ester bath and then dried with a clean absorbing paper, weighed and immediately re-immersed into methyl ester. Time for this procedure was systematically less than 3 min. It was again checked that samples were not mechanically stressed by the vessel. It was assumed that oxidation induced changes in methyl esters composition were negligible within the duration of the experiments.

2.2.2. Permeability measurement

One of the methods classically used for the determination of the coefficient of fluid permeability through polymeric materials (elastomers, thermoplastics...) is the “Weight Loss” method. The method allows the amount of diffusing molecules crossing the material to be determined by the weight loss of a metallic cell containing the fuel of interest and closed by the polymer membrane to be studied (Fig. 1). To carry out the study, this cell is periodically weighed (period of once per day to several times per month according to recorded losses) on a precision balance to follow the global weight loss of the assembly. The Fig. 1 represents experimental curves of weight loss with time. Permeability (denoted by Pe in the following) is estimated from the slope by the formula:

$$ Pe = \frac{m \cdot e}{s} $$

where:
- Pe is expressed in g cm cm$^{-2}$ s$^{-1}$,
- m is the lost mass (in g) during the time duration t (in s),
- e is the polymer thickness (in cm),
- s is the sample surface in contact with methyl ester (in cm$^2$).

3. Results

3.1. Solubility measurements

The kinetic curves of mass uptake are presented in Fig. 2 for PE + rapeseed methyl ester. They display the classical shape with maximal uptake rate at the beginning of exposure which then decreases continuously. A pseudo

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Methyl oleate $w_{eq}$ c (mol l$^{-1}$)</th>
<th>Methyl linoleate $w_{eq}$ c (mol l$^{-1}$)</th>
<th>Rapeseed methyl ester $w_{eq}$ c (mol l$^{-1}$)</th>
<th>Soy methyl ester $w_{eq}$ c (mol l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>0.116 0.666</td>
<td>0.092 0.542</td>
<td>0.095 0.555</td>
<td>0.092 0.539</td>
</tr>
<tr>
<td>60</td>
<td>0.070 0.423</td>
<td>0.064 0.386</td>
<td>0.071 0.425</td>
<td>0.069 0.414</td>
</tr>
<tr>
<td>45</td>
<td>0.056 0.343</td>
<td>0.051 0.312</td>
<td>0.055 0.335</td>
<td>0.054 0.328</td>
</tr>
<tr>
<td>23</td>
<td>0.047 0.288</td>
<td>0.042 0.257</td>
<td>0.047 0.290</td>
<td>0.047 0.291</td>
</tr>
</tbody>
</table>

Fig. 3. $w/w_{eq}$ against $(t^{1/2})/e$ for rapeseed methyl ester sorption into polyethylene 1 at 75 °C (a), 60 °C (b), 45 °C (c) and room temperature (d).
Diffusion coefficients (in cm² s⁻¹) estimated from the slopes of Fig. 4 together with corresponding Arrhenius parameters.

<table>
<thead>
<tr>
<th></th>
<th>75 °C</th>
<th>60 °C</th>
<th>45 °C</th>
<th>25 °C</th>
<th>ln D₀ (D₀ in cm² s⁻¹)</th>
<th>ΔHₒ (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl oleate</td>
<td>2.40 x 10⁻⁷</td>
<td>8.21 x 10⁻⁸</td>
<td>2.36 x 10⁻⁸</td>
<td>1.39 x 10⁻⁹</td>
<td>14.46</td>
<td>85.9</td>
</tr>
<tr>
<td>Methyl linoleate</td>
<td>1.96 x 10⁻⁷</td>
<td>5.02 x 10⁻⁸</td>
<td>2.30 x 10⁻⁸</td>
<td>1.13 x 10⁻⁹</td>
<td>13.43</td>
<td>83.8</td>
</tr>
<tr>
<td>Rapeseed methyl ester</td>
<td>1.82 x 10⁻⁷</td>
<td>6.22 x 10⁻⁸</td>
<td>2.12 x 10⁻⁸</td>
<td>1.26 x 10⁻⁹</td>
<td>12.91</td>
<td>82.3</td>
</tr>
<tr>
<td>Soy methyl ester</td>
<td>2.56 x 10⁻⁷</td>
<td>6.48 x 10⁻⁸</td>
<td>2.10 x 10⁻⁸</td>
<td>1.25 x 10⁻⁹</td>
<td>15.16</td>
<td>88.1</td>
</tr>
</tbody>
</table>
interpreted this result as follows: to the interaction of methyl esters with polar sites (structural irregularities) of PE or the adsorption of dissolved in the apolar regions of PE.

The diffusion of a chemical into a polymer is facilitated by decreasing the penetrant size (expressed by its specific molar volume \( V^* \)) and also increases with increasing free volume \( V_f \), as expressed by the Cohen and Turnbull theory [9]:

\[
D = A \cdot \exp\left(-\frac{\gamma V^*}{V_f}\right)
\]

in which \( \gamma \) is a factor ranging between 0.5 and 1.

This theory has led to very sophisticated theories permitting prediction for cases in which penetrant bring its own free volume, thus facilitating the diffusion, but requiring a huge number of parameters to be determined [10], which seems out of reach for complex mixtures such as biodiesels.

Several models aimed at correlating molar mass of diffusant, temperature and polymer nature have been proposed by Helmroth [11,12], Limm and Hollifield [13], Mercea [14], Piringer [15], and Begley [16]. It is noteworthy that the correlation between ln D and M works particularly well for penetrants having a linear structure [17], which is the case here (some differences appear for polycyclic and branched penetrants molecules, with distortions in the same behavior having been previously observed, for instance by McCall et al [8] for water solubility in PE. The authors interpreted this result as follows:

- the term of lowest activation energy corresponds to the dissolution in the apolar regions of PE;
- the term of the highest activation energy corresponds to the interaction of methyl esters with polar sites (structural irregularities) of PE or the adsorption of methyl esters at the surface of crystalline lamellae.

\[
c = S \times P
\]

where \( P \) (here equal to the saturated vapor pressure \( P_{sat} \) of the methyl ester under study, calculated from methyl ester boiling point \( T_b \) using Antoine’s law:

\[
\log P_{sat} = A - \frac{B}{T} + C
\]

\( P_{sat} \) being expressed here in Pa and \( T \) in K, \( A \), \( B \) and \( C \) coefficient (Table 4) from [6,7]. The values of \( S \) determined for methyl oleate and methyl linoleate are listed in Table 4. An Arrhenius plot of \( S \) is shown in Fig. 7 and may be used as model for solubility of other methyl esters of vegetable oil.

A positive curvature is observed, revealing that the solubility process cannot be represented by a single Arrhenian term. The simplest model could be the sum of two Arrhenian terms:

\[
S = S_{01} \cdot \exp\left(-\frac{\Delta H_{01}}{RT}\right) + S_{02} \cdot \exp\left(-\frac{\Delta H_{02}}{RT}\right)
\]

This behavior has been previously observed, for instance by McCall et al [8] for water solubility in PE. The authors interpreted this result as follows:

- the term of lowest activation energy corresponds to the dissolution in the apolar regions of PE;
- the term of the highest activation energy corresponds to the interaction of methyl esters with polar sites (structural irregularities) of PE or the adsorption of methyl esters at the surface of crystalline lamellae.

It remains, however, to calculate the corresponding 4 parameters, without to our knowledge the existence of reliable structure – solubility relationships in the case of semi-crystalline polymer and liquid penetrants close to the case under study.

4.2. Prediction of diffusivity

Table 3

<table>
<thead>
<tr>
<th>Penetration</th>
<th>Pe (60 °C)</th>
<th>Pe (80 °C)</th>
<th>( \Delta H_{eq} ) (kJ mol(^{-1}))</th>
<th>( \Delta H_{sat} ) (kJ mol(^{-1}))</th>
<th>( \Delta H_D ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl oleate</td>
<td>(1.14 \times 10^{-10})</td>
<td>(1.32 \times 10^{-9})</td>
<td>119.4</td>
<td>24</td>
<td>95.7</td>
</tr>
<tr>
<td>Soy methyl ester</td>
<td>(1.56 \times 10^{-10})</td>
<td>(1.53 \times 10^{-9})</td>
<td>113.6</td>
<td>18.1</td>
<td>93.5</td>
</tr>
<tr>
<td>Rapeseed methyl ester</td>
<td>(1.44 \times 10^{-10})</td>
<td>(9.96 \times 10^{-10})</td>
<td>94.5</td>
<td>17.8</td>
<td>76.7</td>
</tr>
<tr>
<td>30% soy + 70% rapeseed</td>
<td>(9.0 \times 10^{-11})</td>
<td>(9.0 \times 10^{-10})</td>
<td>112.5</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
Table 4
Antoine’s law coefficient for methyl oleate and methyl linoleate.

<table>
<thead>
<tr>
<th></th>
<th>T s (K)</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C18:1</td>
<td>622</td>
<td>9.9155</td>
<td>2583.52</td>
<td>-96.15</td>
</tr>
<tr>
<td>C18:2</td>
<td>639</td>
<td>8.2175</td>
<td>1450.62</td>
<td>-188.03</td>
</tr>
</tbody>
</table>

Arrhenius diagram describing the thermal dependence of diffusivity [18]). The general form of these models is:

\[
D = a_0 \cdot \exp \left( a_1 + a_2 \cdot M^{a_3} + a_4 \cdot \frac{M^{a_5}}{T} \right) \tag{9}
\]

D is expressed in cm² s⁻¹, M in g mol⁻¹ and T in K. Coefficients for LDPE and HDPE are given in Tables 5 and 6.

It seems that diffusion coefficient values and corresponding activation energy for diffusion in polyethylene 1 (Table 2) are conveniently simulated by some of these models, for example Begley’s model for LDPE, which is not surprising for the PE used in this study and also in other semicrystalline polymers [19]). It is in particular noteworthy that those models predict an activation energy ca 85 kJ mol⁻¹ (Fig. 4), in excellent agreement with our experimental results (Table 2).

Table 5
Parameters for molecular models for LDPE.

<table>
<thead>
<tr>
<th></th>
<th>a₀</th>
<th>a₁</th>
<th>a₂</th>
<th>b₂</th>
<th>a₃</th>
<th>a₄</th>
<th>b₄</th>
<th>a₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Begley 10⁴</td>
<td>11.3</td>
<td>-0.1351</td>
<td>2/3</td>
<td>0.003</td>
<td>-10454</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Piringer 10⁴</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>-0.0101</td>
<td>-10450</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Mercea 10⁴</td>
<td>10.6</td>
<td>-0.13</td>
<td>2/3</td>
<td>0</td>
<td>-10450</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Limm exp (-0.9)</td>
<td>0.555</td>
<td>1/2</td>
<td>0</td>
<td>-1140.5</td>
<td>1/3</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7. Arrhenius diagram of S = c/P_{sat} for methyl oleate (■) and methyl linoleate (○).

Fig. 8. Comparison of experimental and ‘predicted’ (see text) permeability values.

4.3. Prediction of the permeability

Measured values for permeability of methyl oleate, soy methyl ester, rapeseed methyl ester and a mix of rapeseed and soy methyl esters are gathered in Table 3. Since:

\[
P_{e} \sim \text{sol} \times D \tag{10}
\]

\[
\Delta H = \Delta H_{p} - \Delta H_{s} \tag{11}
\]

The solubility actually displays curvature in the Arrhenius diagram. However, we will approximate here it to an Arrhenius function in the “high” temperature range (45-75 °C) for roughly estimating \(\Delta H_{s}\).

This result suggests that \(\Delta H_{p}\) is certainly close to 95 kJ mol⁻¹ (Table 4). It corresponds well to the activation energy predicted by molecular models for a HDPE such as polyethylene 2 (see Tables 5 and 6).

It seemed to us interesting to compare the measured values of permeability with a prediction from solubility and diffusivity measured values. To that purpose:

- D was calculated from the model by Begley’s equation using HDPE coefficient (and denoted by \(D_{HDPE}\))
- s was estimated from measured solubility values (see Table 2) corrected for crystallinity by the formula: \(s_{HDPE} = s_{LDPE}\cdot(1 - X_{HDPE})/(1 - X_{LDPE})\) using crystallinity ratio values determined from DSC measurements (see ‘Experimental’ section).

The comparison is presented in Fig. 8. A factor ca 4 is observed between ‘predicted’ and measured permeability values. Even if the agreement between both values can be improved, it seems that the new cell developed for this work is a promising tool for studying permeability of chemicals through polymers.

Table 6
Parameters for molecular models for HDPE.

<table>
<thead>
<tr>
<th></th>
<th>a₀</th>
<th>a₁</th>
<th>a₂</th>
<th>b₂</th>
<th>a₃</th>
<th>a₄</th>
<th>b₄</th>
<th>a₅</th>
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<td>2/3</td>
<td>0.003</td>
<td>-10454</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Piringer 10⁴</td>
<td>8</td>
<td>0</td>
<td>0</td>
<td>-0.0101</td>
<td>-10450</td>
<td>0</td>
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</tr>
<tr>
<td>Mercea 10⁴</td>
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<td>2/3</td>
<td>0</td>
<td>-10450</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Limm exp (-0.9)</td>
<td>0.819</td>
<td>1/2</td>
<td>0</td>
<td>-1760.7</td>
<td>1/3</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5. Conclusions

This paper reports solubility, diffusion and permeability data for two biodiesel compounds (soy and rapeseed methyl esters) and two model systems (methyl oleate and methyl linoleate) in two polyethylenes in the 25-75 °C temperature range. Solubility ranges from c.a. 5% at the lowest temperature to more than 10% at the highest, and diffusion increases from c.a. 10^-9 cm² s⁻¹ at 25 °C to more than 10^-7 cm² s⁻¹ at 75 °C. The corresponding activation energies are close to 85 and 90 kJ mol⁻¹ for diffusion in LDPE and HDPE, respectively, and about 110 kJ mol⁻¹ for permeability in HDPE. These data were used for comparisons with existing predictive models for solubility and diffusivity. In particular, curvature observed in the Arrhenius diagram of solubility was satisfyingly modeled by modifying the Henry's law by supposing a dual dissolution process in polyethylene. It was also checked that some molecular models based on correlation between diffusion coefficient, temperature and penetrant molar mass can simulate the measured diffusion coefficients. A new device was employed for measuring fuel permeability through polymers. Its measurements were tentatively validated from comparisons with the above reported values. It showed that biodiesels are less aggressive towards PE than mineral ones.

Acknowledgments

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References