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Kinetics of interaction of palm ethyl biodiesel with three different polymer materials

Giselle Lutz[a] and Julio F. Mata-Segreda[a*]

Diesel diffuses into neoprene matrices 10% faster than palm ethyl biodiesel at 20°C. In contrast, the palm biodiesel soaks highly plasticized PVC five times faster than diesel. Phthalate plasticizer leaks from the PVC matrix 14 times faster when biodiesel is the absorbed liquid, relative to petrodiesel. This biodiesel penetrates polybutadiene-styrene resins at rates that depend on the ratio of phenyl to CH═CH units in the resins. Copyright © 2008 John Wiley & Sons, Ltd.

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INTRODUCTION

Reservoirs, pipes and fittings made of thermoplastic materials are widely used in industries where storage and conveyance of liquids requires high-quality construction materials, featuring excellent corrosion resistance. Stainless steel, coated steel, glass and ceramic materials can often be advantageously replaced by thermoplastic materials, thus ensuring safety, reliability and economic benefits under similar operating conditions.

The deleterious effect of liquids on plastics and elastomers can be explained by the following sequence of events: swelling of the polymer matrix, leaching of plasticizers from the solid and the actual dissolution of the polymer itself.

Plastic equipment adequate for hydrocarbon fuel handling may not necessarily be adequate for the case of fatty esters (biodiesel). This situation poses a safety threat in garages and farms where this kind of material is used not only as fuel, but also as cleaning fluid and lubricant. A great deal of qualitative information can be found on the compatibility of biodiesel with polymer materials.[1–6]

The rate factor in liquid–polymer interaction is important for the safety aspects of biodiesel handling (containers, hoses, fittings, stopcocks, etc.). Thus, studies on the kinetics of absorption of biodiesel by polymer matrices were deemed desirable. Numerical data on the interaction of liquid bio-organic materials with plastics and elastomers are useful, because they allow the establishment of accurate safety regulations for the handling of these liquids.

We report on the absorption of palm ethyl biodiesel by three different types of polymer materials: neoprene, polybutadiene-styrene polymer (high-impact polystyrene, HIPS) and highly plasticized PVC.

Diffusion through the absorbent matrix

The process of diffusion of a mobile species in and through an absorbing solid of certain shape and dimensions is described by Fick's second law:

$$\frac{\partial C}{\partial t} = D^i \nabla^2 C \qquad (1)$$

where C is the concentration of the diffusing species at some point in the solid matrix at time t, and D^i is its apparent internal diffusion coefficient. This definition of D^i implies isotropic nature of the diffusion process. When the concentration of the mobile species at the liquid–solid interphase is constant (C_0), integration of Eqn (1) yields the following working solution, along each of the Cartesian coordinates ($q = x$, y or z):[7]

$$C(q,t) = C_o erfc\left(\frac{q}{\sqrt{4D^i t}}\right) \qquad (2)$$

where the *erfc* symbol stands for the *complementary error function*.

The quantity $\sqrt{4D^i t}$ is called the *diffusion length* and gives a measure of how far the concentration of the mobile species has propagated in the q direction by diffusion in time t.

The degree of saturation of the solid matrix by the diffusing species can be defined as $F = \bar{C}(t)/\bar{C}(\infty)$, where $\bar{C}(t)$ is the mean concentration of the mobile species within the matrix volume (V) at time t and $\bar{C}(\infty)$ is the concentration at equilibrium. Thus, $\bar{C}(t) = 1/V \int_V C(V,t)\mathrm{d}V$.

The particular algebraic formulas for the relationship between F and t are different for spherical particles, plates, rods or any other geometry. Those particular expressions incorporate the geometrical features of the absorbing bodies such as radii, cross-sectional diameters, and thickness.

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* *Correspondence to: J. F. Mata-Segreda, Laboratory of Bio-organic Chemistry, School of Chemistry, University of Costa Rica, 2060 Costa Rica.*
E-mail: julio.mata@ucr.ac.cr; jmata@cariari.ucr.ac.cr

a *G. Lutz, J. F. Mata-Segreda*
Laboratory of Bio-organic Chemistry, School of Chemistry, University of Costa Rica, 2060 Costa Rica

For times shorter than equilibrium periods, one obtains the general relation:

$$\lim_{t \to 0} F = \sqrt{\text{Geometric factor} \times D^i \times t} \qquad (3)$$

where F is the fractional attainment of equilibrium at time t. Experiments carried out with different liquids on solid samples of polymers with the same geometrical features provide the means of obtaining relative values of D^i, by comparison of the slopes in F *versus* $\sqrt{t}$ plots. Indeed, linearity of $F - \sqrt{t}$ data indicates conformity of the data with Fick's second law.

RESULTS AND DISCUSSION

Neoprene

The value of the Hildebrand solubility parameter of neoprene is $\delta_H = 18.4\ (\text{J cm}^{-3})^{½}$.[8] The δ_H values of petrodiesel and palm ethyl biodiesel are $16.6 \pm 0.2\ (\text{J cm}^{-3})^{½}$ and $17.3 \pm 0.6\ (\text{J cm}^{-3})^{½}$, respectively.[9] The two liquids have δ_H lower than neoprene. None of the two liquids is expected either to dissolve or degrade the elastomer, but swelling of the polymer matrix is the process expected.

The neoprene gaskets of the same size and shape were immersed in glass beakers containing the particular liquid of interest. The inorganic filler in the elastomer accounted for 5.4% ash. The amounts of total swelling (mass wise) at equilibrium were 189% for diesel and 97% for palm ethyl biodiesel. Table 1 gives the rate equations and the D^i value relative to petrodiesel, and includes the observations for palm olein and brake fluid.

The neoprene tubing was cut into square pieces with total 30 cm^2 surface area. The amount of filler in this material accounted for 48.7% ash. The degree of swelling at equilibrium for diesel was 107 and 93% for biodiesel. The degree of swelling is now different for diesel, due to the different relative amounts of neoprene and inorganic filler in the two materials (neoprene-rich hydraulic brake gasket *vs*. hose). F *versus* $\sqrt{t}$ data for the absorption experiments with petrodiesel and biodiesel are shown in Figures 1 and 2, respectively. The Fickian expressions are as follows:

$$\text{(a) biodiesel} \quad F = (1.20 \pm 0.01) \times 10^{-3}\, s^{-1/2} \sqrt{t}, \quad r^2 = 0.997$$

$$\text{(b) petrodiesel} \quad F = (1.25 \pm 0.02) \times 10^{-3}\, s^{-1/2} \sqrt{t}, \quad r^2 = 0.996$$

Data reduction according to Eqn (3) gives $D^i_{\text{Biodiesel}}/D^i_{\text{Diesel}} = 0.92 \pm 0.01$. This value is identical to the quotient observed with the gasket material, $D^i_{\text{Biodiesel}}/D^i_{\text{Diesel}} = 0.89 \pm 0.03$.

Table 1. Rate equations for the diffusion of the organic liquids into neoprene gaskets, $T = 20°\text{C}$

Liquid	Rate equation	D^i/D^i_{Diesel}
Brake fluid	$F = \text{Zero}$	Zero
Palm triacylglycerol	$F = \text{Zero}$	Zero
Petrodiesel	$F = (1.23 \pm 0.03) \times 10^{-3}\, s^{-½}\sqrt{t}$	1
Palm ethyl biodiesel	$F = (1.10 \pm 0.03) \times 10^{-3}\, s^{-½}\sqrt{t}$	0.89 ± 0.03

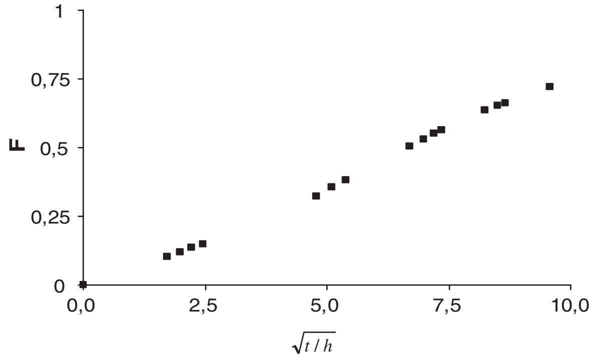

Figure 1. Absorption of petrodiesel by a neoprene matrix at 20°C

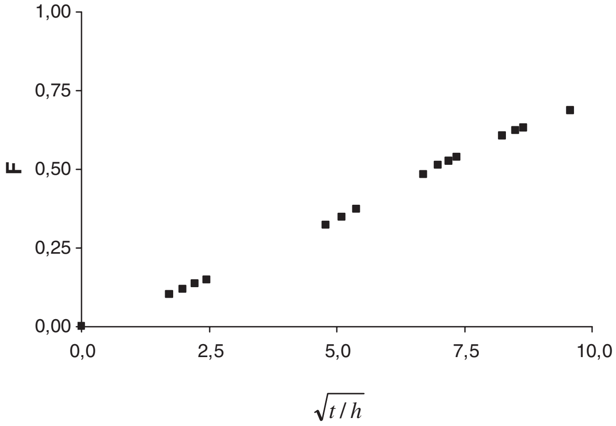

Figure 2. Absorption of palm ethyl biodiesel by a neoprene matrix at 20°C

It is interesting to point to the result that the relative diffusion of biodiesel in neoprene matrices is nearly independent of the amount of inorganic filler used in their formulation.

Though biodiesel diffuses 10% slower than petrodiesel in neoprene matrices, care must be taken in avoiding the use of common industrial neoprene hoses for the conveyance of either biodiesel or petrodiesel.

Common brake fluids are materials made of polyalkylene glycol ethers. The polarity of these materials correlates well with its lack of penetration into the neoprene matrix. This solubility feature is also reflected in the difference between the average value of Hildebrand δ_H for different glycol ethers $[20\ (\text{J cm}^{-3})^{1/2}]$[10–12] and the value for neoprene $[18.4\ (\text{J cm}^{-3})^{1/2}]$.[8]

The palm TAG is less polar than brake fluid, but does not penetrate the synthetic rubber matrix either, probably due to steric reasons. The apparent molar volume of the oil can be calculated from its mean molecular weight and density.[13] The palm TAG has 0.92 dm^3/mol, a value about three times greater than for palm ethyl biodiesel (0.34 dm^3/mol). Again, a difference is also observed in the δ_H values of neoprene (18.4) and the estimated value for the TAG (13).[14]

Plasticized PVC

The tubing sample was cut into square pieces of 13 cm^2 total surface area. The solubility parameter of PVC materials is of the order of $20\ (\text{J cm}^{-3})^{½}$.[10–12] Figure 3 shows clearly both the swelling process and the leaching of the phthalate plasticizer, from the solid matrix to the outer petrodiesel or biodiesel phases.

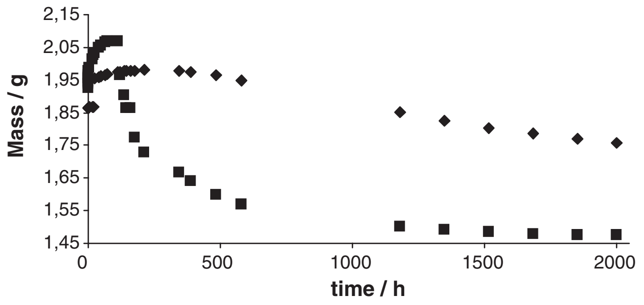

Figure 3. Absorption of petrodiesel (◆) and palm ethyl biodiesel (■) by highly plasticized PVC at 20°C

Table 2. Initial fluxes of different biodiesel samples into a highly plasticized PVC matrix, $T = 20°\mathrm{C}$

Liquid	$\lim_{t\to 0}\frac{\mathrm{d}m/\mathrm{d}t}{\mathrm{Area}}\,(\mathrm{g\,h^{-1}\,m^{-2}})$
Petrodiesel	5.4 ± 0.6
Palm ethyl biodiesel	24 ± 5

Fitting of the initial m-time data points to Eqn (3) would lack precision because, the corresponding m_∞ values are at best difficult to determine, due to the counter flow of plasticizer and entering liquid. Therefore, Table 2 gives initial flux values rather than diffusion coefficients. The result is now opposite to the observation in the case of neoprene. Biodiesel enters the polymer matrix about five times faster than petrodiesel.

The overall mass loss of the PVC sample is 20% after 3 months of immersion in biodiesel and 6% in the case of petrodiesel. The descending parts of the two curves fit well a monoexponential decay rate equation. Table 3 shows the specific rates of plasticizer loss ($k = (-\mathrm{d}m/(m - m_\infty))/\mathrm{d}t$). Fatty-ester promotion of plasticizer loss is 14 times faster than the action of petrodiesel.

Kim *et al.*[15] reported that the rate of migration of di-(2-ethylhexyl) phthalate [$\delta_\mathrm{H} = 16.2(\mathrm{J\,cm^{-3}})^{1/2}$],[10–12] from highly plasticized PVC sheets to acetonitrile or aqueous ethanol, obeyed a $t^{½}$ law. The leaching process was faster and greater when polar acetonitrile was the absorbed liquid. Our observation for the case of petrodiesel and biodiesel is analogous to the results reported by those authors.

Neither liquid in their experiments soaked the polymer matrix as thoroughly as petrodiesel or biodiesel. The swelling pressure developed inside the polymer matrix in our case, is likely to act as a significant driving force for the migration of the phthalate plasticizer. As the plasticizer leaks, the mechano-chemical potential inside the matrix decreases and so does the rate of leakage, in contrast to Fickian behaviour which depends only on concentration gradients. This must show itself as obedience of the system to a first-order kinetic scheme.

Table 3. First-order rate constants for the migration of plasticizer from a PVC matrix, 20°C

Liquid	$10^3\,k\ (\mathrm{h^{-1}})$
Petrodiesel	0.34 ± 0.01
Palm ethyl biodiesel	4.9 ± 0.7

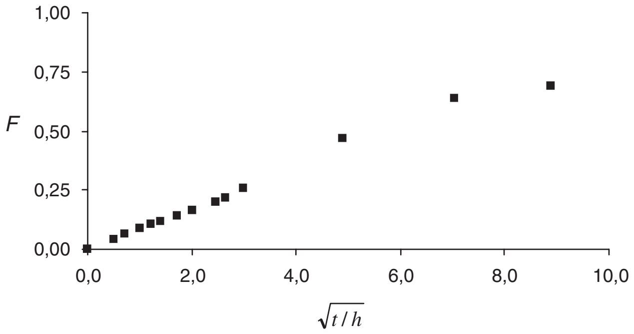

Figure 4. Absorption of palm ethyl biodiesel by HIPS resin A at 20°C

After 3 months, the final effect of the action of petrodiesel and biodiesel on the highly plasticized PVC is the transformation of the flexible material into a rigid brittle material, due to crystallization of the polymer in the absence of the plasticizer. The phenomenon though well known qualitatively, can now be considered in terms of quantitative mean leaching times ($1/k$); 2.9×10^3 h for the action of petrodiesel and 2.0×10^2 h for palm ethyl biodiesel.

HIPS resins

These materials are microscopic 'two-phase' systems where polybutadiene-rich (PB) particles are embedded in a larger polystyrene matrix (PS). The solubility parameter of polybutadiene-styrene resins is around 19 $(\mathrm{J\,cm^{-3}})^{½}$.[8,10–12] Again, it is expected that swelling of the solid material occurs with both biodiesel and petrodiesel. Figures 4 and 5 show the $F - \sqrt{t}$ data for the absorption of biodiesel into two different HIPS resins, A and B. The rate equation for the case of resin A is $F = (1.40 \pm 0.02) \times 10^{-3}\,s^{-½}\sqrt{t}$ and for resin B, the equation is $F = (1.27 \pm 0.02) \times 10^{-3}\,s^{-½}\sqrt{t}$. The quotient $D^i_\mathrm{Biodiesel}$(in A)/$D^i_\mathrm{Biodiesel}$(in B) $= 1.22 \pm 0.02$ results from the empirical equations. The observed difference must be due to differences in composition of the resin materials.

The proton NMR spectra of the resins were obtained ($\mathrm{Cl_3CD}$, 400 MHz Varian Mercury). The solubility of HIPS materials in chloroform is possible due their identical Hildebrand solubility parameters; 19 $(\mathrm{J\,cm^{-3}})^{1/2}$ for the resins and 18.7 $(\mathrm{J\,cm^{-3}})^{1/2}$ for chloroform. A laboratory sample of linear PS showed multiple-absorption patterns in the range δ 6.3–7.2 (phenyl protons, total integration 5.44) and in the range δ 1.4–2.1 (aliphatic protons, total integration 3.05). Integration agrees with the 5:3 ratio expected for the linear polymer structure.

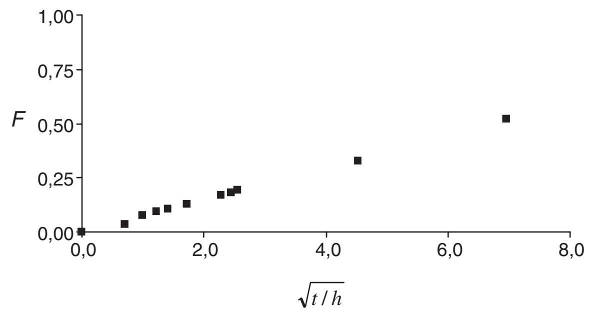

Figure 5. Absorption of palm ethyl biodiesel by HIPS resin B at 20°C

The spectrum of resin A shows the same multiple signals in δ 6.3–7.2 (integration 3.61) and δ 1.4–2.1 (integration 2.70) but also signals at δ 0.9 (aliphatic, integration 0.13) and at δ 5.4 (vinyl, integration 0.03). The vinyl protons are indicative of the remaining carbon–carbon double bonds in the polybutadiene chains. The ratio of phenyl moieties to residual CH=CH was calculated as $(3.61/5)/(0.03/2) = 48$. The spectrum of resin B shows the multiple signals in δ 6.3–7.2 (integration 4.25), δ 1.4–2.1 (integration 2.75), δ 0.9 (integration 0.15) and δ 5.4 (integration 0.10). The ratio of phenyl moieties to residual CH=CH was calculated as $(4.25/5)/(0.10/2) = 17$. Resin A has greater phenyl/CH=CH ratio than resin B.

The macroscopic (kinetic) result is that diffusion of biodiesel molecules is faster, the larger the relative amount of styrene units.

Maddinelli *et al.*[16,17] studied the interaction of hydrocarbons with composite polymers by NMR techniques. They found an increase in relaxation times of the PB rubber phase protons in HIPS after solvent exposition (c-C_6D_{12}, C_4Cl_6, c-C_5H_{10}), thus suggesting an increase in the molecular mobility of the two phases of the polymer.

The result suggests that the PB particles in HIPS pose an obstructive effect to the diffusion of biodiesel molecules through the resin matrix.

The rate data in this work is part of a data base under construction that aims to allow quantitative rate predictions of the effect of energy biomaterials on elastomers and resins. Quantitative information and its molecular correlation are needed to establish accurate safety regulations for the handling of this kind of biomaterials.

CONCLUSIONS

The following conclusions are drawn from the experimental results:

1. The penetration of liquids into the polymer matrices studied obeys Fick's second law.
2. Petrodiesel diffuses faster in neoprene matrices than palm ethyl biodiesel.
3. Palm ethyl biodiesel diffuses faster in highly plasticized PVC matrices than petrodiesel.
4. Palm ethyl biodiesel promotes the migration of phthalate plasticizer from the PVC material 14 times more intensely than petrodiesel.
5. The rate of diffusion of palm ethyl biodiesel in polybutadiene-styrene resins depends on the ratio of phenyl to CH=CH moieties.

EXPERIMENTAL

Materials

Highly plasticized PVC Tygon® R-3603 tubing (27 mm external diameter, 20 mm internal diameter) and neoprene tubing (25 mm external diameter, 20 mm internal diameter) were obtained from the stockroom. Neoprene hydraulic brake gaskets (Seiken® JIS D2605, 7.4 mm internal diameter) were obtained from a local auto-part dealer. Two HIPS resins used for the making of containers for dairy products were used in this study.

Palm ethyl biodiesel was synthesized in the laboratory, by the usual method of transesterification of oils (triacylglycerol, TAG) with either methanol or ethanol (NaOH as catalyst).[9]

Palm olein was a gift from Palmatica, Costa Rica. Brake fluid (Prestone®, polyalkylene glycol ethers) was obtained from a local auto-part dealer.

Rate measurements

The materials were cut into convenient square pieces of different surface areas. The hydraulic brake gaskets were used as such. The solid samples were immersed in 50 cm^3 of the particular liquid under study. The samples were removed at regular intervals, and the surface-adhered liquid drops were wiped by carefully pressing the samples in between paper towel and weighed on a digital balance. The kinetic parameters were determined by linear fitting of F *versus* $\sqrt{t}$ data according to Eqn (3), where $F = (m - m_0)/(m_\infty - m_0)$. The experiments were carried out in a temperature-controlled room at 20 ± 2°C.

The rate of leaching of phthalate plasticizer from the PVC matrices was calculated by fitting m-time data to a first-order rate law, by nonlinear least-squares fitting.

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