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Fatty Acid Methyl Esters as Biosolvents of Epoxy Resins: A Physicochemical Study

Y. Medina Gonzalez · P. de Caro · S. Thiebaud-Roux · C. Lacaze-Dufaure

Abstract The C8 to C18 fatty acid methyl esters (FAME) have been compared as solvents for two epoxy resin pre-polymers, bisphenol A diglycidyl ether (DGEBA) and triglycidyl *p*-aminophenol ether (TGPA). It was found that the solubilization limits vary according to the ester and that methyl caprylate is the best solvent of both resins. To explain these solubility performances, physical and chemical properties of FAME were studied, such as the Hansen parameters, viscosity, binary diffusion coefficient and vaporization enthalpy. Determination of the physicochemical parameters of FAME was carried out by laboratory experimentations and by calculation from bibliographic data. The Hansen parameters of FAME and epoxy resins pre-polymers were theoretically and experimentally determined. The FAME chain length showed a long dependence on the binary diffusion parameters and kinematic viscosity, which are mass and momentum transport properties. Moreover, the vaporization enthalpy of these compounds was directly correlated with the solubilization limits.

Keywords Biosolvents, FAME · Epoxy · Resins · Surface cleaning · Physicochemical parameters · Hansen parameters · Dipole moment

1 Introduction

In recent years, more and more constraining environmental regulations have been adopted to limit the use of industrial solvents like methyl ethyl ketone, perchloroethylene and other halogenated solvents responsible for VOC emission and greenhouse gas production. As a result, biosolvents have attracted more attention as alternatives to these commonly used solvents [1, 2].

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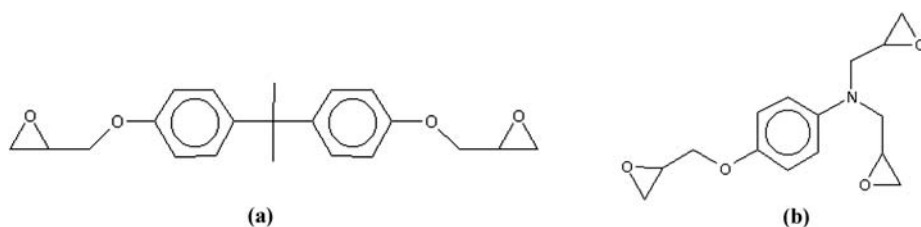


Fig. 1 a Bisphenol A diglycidyl ether (DGBA); b triglycidyl *p*-aminophenol ether (TGPA)

Fatty acid methyl esters (FAME) are considered to be environmentally friendly bio-solvents due to their high biodegradability, their low toxicity, their low vapor pressure and non-inflammability [3, 4]. These remarkable characteristics encouraged us to study their performances as alternative solvents for epoxy resins pre-polymers.

Epoxy resins pre-polymers are widely used in industry as basic monomers for the production of two major polymers: epoxy resins and polycarbonates. These polymers are used in several industrial sectors such as the petrochemical and energy fields, packaging, restoring, panels and composites, adhesives, sealants and the ship building industry. These applications involve cleaning of manufacturing and conditioning materials using common solvents like acetone and methyl ethyl ketone. This study deals with the cleaning of bisphenol A diglycidyl ether (DGEBA) and triglycidyl *p*-aminophenol ether (TGPA) from metal surfaces by using fatty acid methyl esters.

Chemical structures of the pre-polymers tested in this study are shown on Fig. 1. With the aim of explaining the observed solubility behavior, the Hansen solubility parameters were first determined for the epoxy resin pre-polymers and the fatty C8 to C18 acid methyl esters.

In the thermodynamics of solutions, the Hansen solubility parameters have been conveniently used to estimate the solubility or miscibility between two compounds [5, 6]. These parameters are frequently applied to formulations of products in cosmetics, paints or polymer blends [7].

Hansen has extended the theory developed by Hildebrand to polar and associated compounds by dividing the solubility parameter (δ) into several partial parameters [3, 4]. The first parameter, δ_d , is related to dispersion forces, the second one, δ_p , to polar forces, and the last one, δ_h , to specific interaction forces (such as hydrogen bonding, acid/base interactions, etc.).

Actually, the δ_p parameter takes into account dipole–dipole, dipole–induced dipole and charge–dipole interactions between the molecules, whereas δ_d takes into account all the non-specific interaction forces between molecules.

These three parameters are connected to a total parameter δ (similar to the Hildebrand parameter) through Eq. 1.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (1)$$

The Hansen parameters were experimentally determined as follows. Solubility tests were conducted with epoxy resin pre-polymers and FAME in 40 solvents. These results were used to generate the Hansen solubility sphere and to obtain the solubility parameters, designated by the center of the sphere. Theoretical Hansen parameters were obtained by a group contribution method [8]. Other physicochemical parameters, such as the binary diffusion parameters, kinematic viscosities and vaporization enthalpies (for the cohesion energy between solvent molecules) were used to explain the performances of these solvents.

2 Experimental Section

Bisphenol A diglycidyl ether (99%), triglycidyl *p*-aminophenol ether (99%) and the fatty acid methyl esters were furnished by Sigma and were used without further purification.

Tests of solubility were performed as follows. Epoxy resins were solubilized in the C8–C18 methyl esters at 50 °C until saturation was reached. These solutions were placed at 25 °C for 48 hrs and the supernatants were then analyzed with the aid of an HPLC apparatus equipped with a UV detector (at a wavelength of 250 nm).

Forty well-known solvents [8] were used for determination of the Hansen parameters of methyl esters and epoxy resin pre-polymers. Tests of the solubilization of DGEBA and TGPA in FAME were carried out at 25 °C at the ratio 50/50 v/v. Solubilization parameters of these solvents were placed into Hansen's three-dimensional space in order to differentiate their solubilizing capability.

A program created on Matlab was used to determine the center and radius of Hansen's sphere of a compound. Equations used to obtain the sphere's radius and the center [9] are:

$$\delta_{xP} = \sum \delta_{xS} / N \quad (2)$$

$$R = \text{Max} \sum [(\delta_{xS} - \delta_{xP})^2]^{1/2} \quad (3)$$

where δ_{xP} is the Hansen parameter of the compound ($x =$ dispersion, polar or hydrogen bonding), δ_{xS} is the Hansen parameter of the solvent capable of solubilizing the compound ($x =$ dispersion, polar or hydrogen bonding), R is the solubility sphere radius, N is the number of solvents ($N = 40$ in the present study).

As can be seen from Eq. 3, the Hansen sphere radius is the distance from the center of the sphere to the farthest solvent capable of solubilizing the studied compound.

Thus, the sphere encloses all the solvents capable of solubilizing the compound, where the solvents incapable of solubilizing it are located outside the sphere. The calculation program also allowed superposition of the spheres.

The dynamic viscosities of FAME were measured by using a controlled stress CSL 100 CARRIMED rheometer at 20 °C.

The binary diffusion parameters of epoxy resins in methyl esters were calculated using the Wilke-Chang equation [7] and are related to the FAME hydrocarbon chain length.

To assess the cohesion energies between solvent molecules, the FAME vaporization enthalpies were measured using a Perkin Elmer calorimeter.

DFT (Density Functional Theory) calculations were performed on the DGEBA and TGPA molecules. In this study, the exchange part of the functional was treated with Becke's three-parameter function (B3) [10]. The correlation part is described by the Lee, Yang and Parr function (LYP) that includes both local and non-local terms [11]. The so-called B3LYP function has proven suitable for describing such systems. The C, N, O and H atoms are treated with the D95 full DZ basis set (LANL2DZ) [12].

All structures presented here were fully optimized using conjugate gradient methods without constraints, and the GAUSSIAN 03 software package [13]. The optimization step was followed by a Mulliken population analysis of the atomic charge and spin density on each atom. The DFT calculations allowed estimation of the dipolar moments of DGEBA and TGPA as the first derivative of the energy with respect to an applied electric field. The stationary points found by the geometry optimization were characterized as minima by computation of the Hessian matrix.

3 Results and Discussion

Concentrations of the saturated solutions of the two prepolymers in FAME are presented in Table 1. These results show that the concentration at the saturation point decreases as the hydrocarbon chain length increases. Only methyl oleate showed a non-typical behavior due to the specific interactions conferred by mono-undersaturation. Methyl palmitate and methyl stearate (C16 and C18) were not tested due to them being solid at ambient temperature.

Hansen's spheres for DGEBA and TGPA and their experimental solubility parameters are shown in Fig. 2. As can be observed, δ_d and δ_p are very similar for both pre-polymers. The differences between the two values are too small to explain the solubility differences, even if δ_h has a higher value for DGEBA. The solubility sphere radius for DGEBA is almost twice that of TGPA, which means that DGEBA is solubilized by a larger number of solvent molecules compared to the TGPA prepolymer.

Two superpositions of the FAME and pre-polymers solubility spheres are shown in Fig. 3. The resin spheres are systematically included in the FAME spheres, which means, according to Hansen's theory, both pre-polymers should be completely solubilized by the tested fatty acid methyl esters. However, total solubilization is not observed experimentally.

Table 1 Concentrations of DGEBA and TGPA in FAME saturated solutions (concentrations in units of $\text{g}\cdot\text{ml}^{-1}$, ± 0.01)

	1	2	3	4	5
	Methyl caprylate (C8)	Methyl laurate (C12)	Methyl myristate (C14)	Methyl oleate (C18:1)	Methyl linoleate (C18:2)
DGEBA	0.58	0.20	0.08	0.14	0.05
TGPA	0.57	0.10	0.04	0.08	0.06

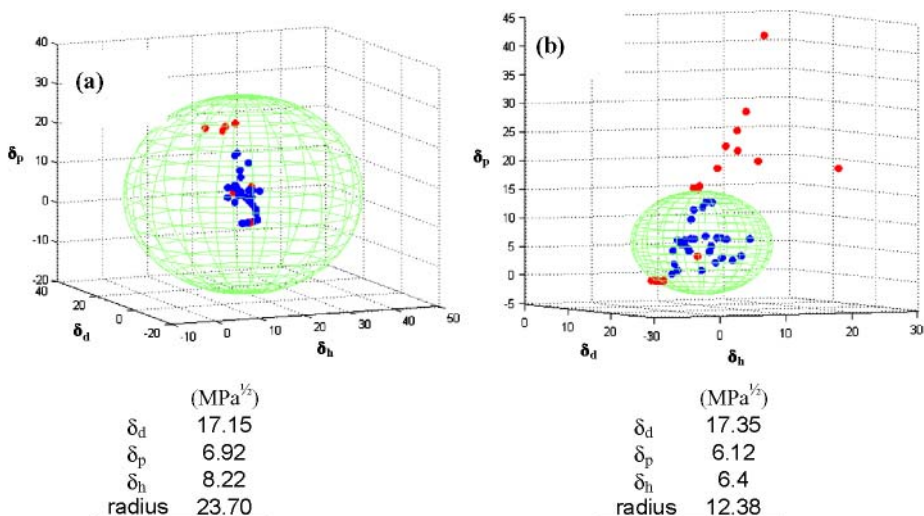
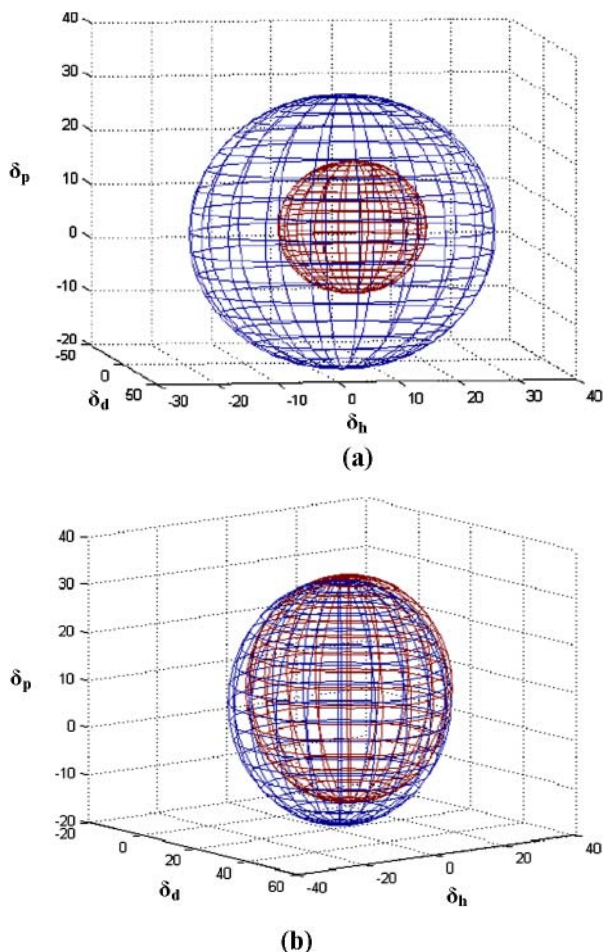


Fig. 2 Hansen's spheres and solubility parameters for DGEBA (a) and TGPA (b)

Fig. 3 Superposition of FAME sphere with the inner sphere of DGEBA (a) and TGPA (b)



Finally, the forty solvents that were used to determine the experimental Hansen parameters do not allow discrimination between the chain length of the esters.

The fatty acid methyl esters studied represent a range of hydrocarbon chain lengths, from C8 to C18, which should confer different polar and dispersion parameter values for each ester. Nevertheless, the experimental method used to obtain FAME Hansen parameters leads to similar values for δ_p , δ_d and δ_h of the FAME. Therefore, it was interesting to test the group contribution method proposed by Krevelen [14] to calculate Hansen parameters (Table 2).

Small differences were obtained for the theoretical Hansen solubility parameter values as the hydrocarbon chain length of the fatty acid methyl esters increases. As expected, the polar parameter (δ_p) of methyl esters is very low, in contrast with the high δ_p values of both resins. Moreover, the polar parameter of FAME changes little with alkyl chain length, as the dipole moment of FAME molecules mainly results from the dipole moment of the carbonyl group [15–19].

The hydrogen bonding parameter (δ_h) of fatty acid methyl esters has a low value due to the low capacity of the molecules to participate in hydrogen bonding. Actually, the two oxygen atoms of the ester functional group and the absence of an electropositive hydrogen

Table 2 Hansen parameters of the studied compounds obtained by the van Krevelen group contribution method [14]

	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	Distance between FAME-DGEBA spheres centers	Distance between FAME-TGPA spheres centers
Methyl caprylate	16.58	2.4	5.85	13.09	13.09
Methyl laurate	16.54	2.06	5.43	13.53	13.55
Methyl myristate	16.51	1.81	5.08	13.88	13.90
Methyl palmitate	16.48	1.61	4.8	14.16	14.19
Methyl stearate	16.46	1.45	4.56	14.40	14.43
Methyl oleate	16.45	1.49	4.61	14.35	14.38
Methyl linoleate	16.45	1.53	4.67	14.29	14.32
Bisphenol A	21.9	13.58	10.09	–	–
Diglycidyl ether					
Triglycidyl	22.84	12.69	10.98	–	–
<i>p</i> -aminophenol ether					

atom within the molecule are not favorable for hydrogen bonding. Among the Hansen parameters, the dispersion parameter values (δ_d) proved to be the most important attractive factor for FAME and resins molecules. These interactions arise from induced dipoles and their strength is related to the polarizabilities of the molecules. In our case, both prepolymers present highly polarizable aromatic rings that are reflected by the high values of δ_d . In the case of FAMES, the polarizabilities of the molecule are close no matter the alkyl chain length, which explains the observed small effect on δ_d .

Distances between the sphere centers of the FAME/resins showed a small increase with the ester hydrocarbon length chain. Among the liquid FAMES, methyl oleate and methyl linoleate show the longest distances.

As can be observed in Fig. 4, a correlation exists between the solubility sphere centers and the solubility limits, including for the undersaturated FAME. For both resins, a solubilization decrease is observed as the distance between the spheres centers increases. Data provided by Hansen theory are thus representative of the experimental solubility results according to the obtained correlation curve.

Figure 5 relates solubilization limits *versus* the dynamic viscosity of FAME. Viscosity is a property associated with local friction between moving molecules. As can be observed in Fig. 5, the kinematic viscosity of FAME increases as the solubility limit diminishes. This phenomenon can be explained by the steric hindrance of long (solvent) molecules, which inhibits the motion of these molecules from solvent bulk to the pre-polymer surface where solubilization takes place.

Solubilization limits as a function of the binary diffusion coefficients are presented on Fig. 6.

According to the correlation, high binary diffusion coefficients contribute to a better solubilization of DGEBA and TGPA in FAME. As known, binary diffusion coefficients are lower for molecules with longer hydrocarbon chain lengths. Solubilization is thus favored for short FAME molecules.

The pre-polymer concentrations at solution saturation are shown on Fig. 7 as a function of the vaporization enthalpy. Esters with the lowest evaporation enthalpy showed the high-

Fig. 4 Concentration at saturation as a function of distance between the FAME and pre-polymer solubility spheres centers: 1, methyl caprylate; 2, methyl laurate; 3, methyl myristate; 4, methyl oleate; 5, methyl linoleate

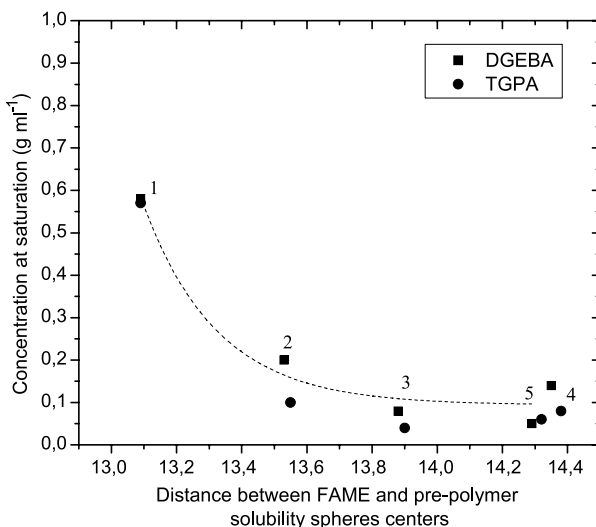
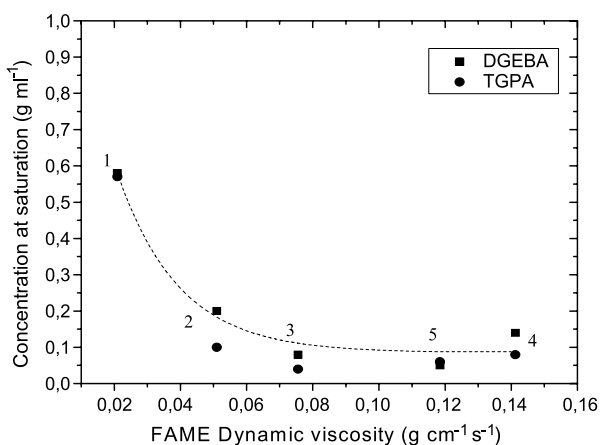


Fig. 5 Concentration of saturated solutions of DGEBA and TGPA in FAME as a function of the dynamic viscosities of FAME: 1, methyl caprylate; 2, methyl laurate; 3, methyl myristate; 4, methyl oleate; 5, methyl linoleate



est concentrations of solubilized pre-polymer. This behavior is a consequence of the direct correlation between evaporation enthalpy and cohesion energy between molecules. Strong solvent–solvent interactions penalize solvent–solute interactions, resulting in a decrease of solubility.

DFT calculations were performed for the TGPA and DGEBA molecules. The optimized geometry of each molecule is presented in Fig. 8. Some geometrical parameters are also presented (bond lengths in Å, angles in degree). The two branches of the DGEBA molecule are geometrically similar with a C1–C2–C3 angle equal to 110.2°. For the TGPA compound, the ternary amino function is nearly planar (dihedral angle = -5.3°). This figure shows a larger steric hindrance for TGPA than for the DGEBA pre-polymer. The DGEBA molecule thus has a more accessible surface for FAME molecules, which means that DGEBA will be more easily solvated by FAME molecules compared to TGPA.

Moreover, these calculations gave the highest dipole moments for TGPA ($\mu = 6.55$ D) and for DGEBA ($\mu = 5.14$ D), compared to values for methyl esters that are close to 1 D [20]. This result is in agreement with the polar parameters δ_p obtained with Hansen's theory.

Fig. 6 Concentration of saturated solutions of DGEBA and TGPA in FAME as a function of the binary diffusion coefficient: 1, methyl caprylate; 2, methyl laurate; 3, methyl myristate; 4, methyl oleate; 5, methyl linoleate

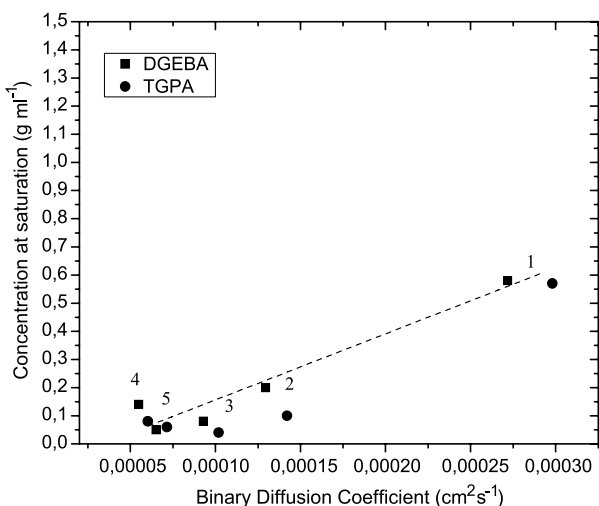
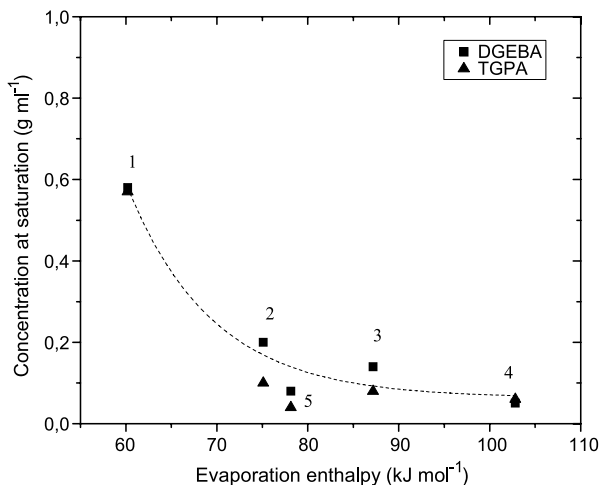


Fig. 7 Concentration at saturation as a function of evaporation enthalpy for solutions of DGEBA and TGPA in FAME: 1, methyl caprylate; 2, methyl laurate; 3, methyl myristate; 4, methyl oleate; 5, methyl linoleate



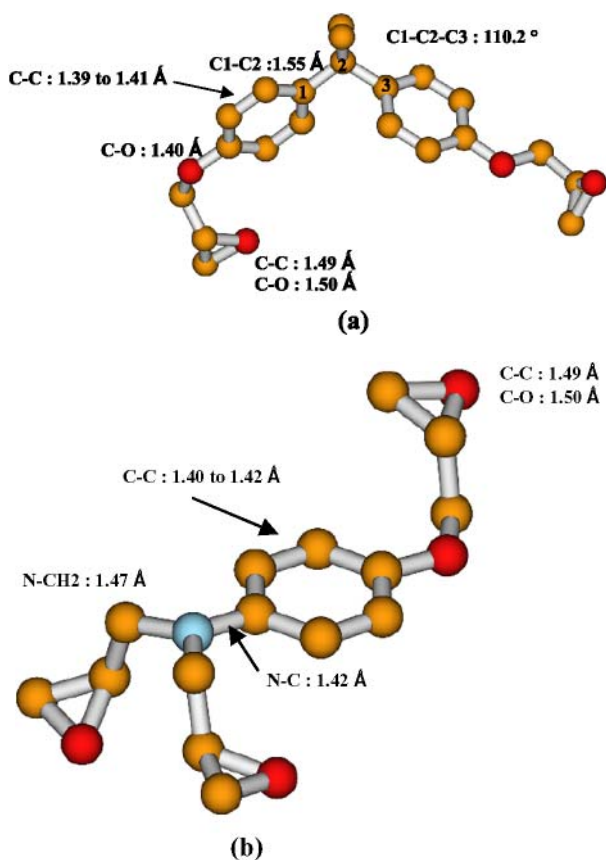
The difference between dipole moments [$\mu(\text{resine}) - \mu(\text{ester})$] is at a minimum for DGEBA, which corresponds to the better affinity between DGEBA and FAME and to the highest solubility limits for this resin.

Consequently, we can conclude that both the polarity and spatial configurations of pre-polymer molecules are involved in the process of solubilization.

4 Conclusion

FAME Hansen parameters determined by experimentation showed no variation with the increase of hydrocarbon chain length. Nevertheless, the Hansen parameters determined by the group contribution method are shown to be capable of taking into consideration the hydrocarbon chain length contributions from the polarizability and dipole moment.

Fig. 8 Spatial representation of pre-polymer molecules according to B3LYP/LANL2DZ calculations: **a** bisphenol A diglycidyl ether (DGEBA); and **b** triglycidyl *p*-aminophenol ether (TGPA)



It was found that the distance between the solubility spheres is a parameter that can be correlated to the experimental solubility limits for the tested FAME series.

Moreover, the solubilization of DGEBA and TGPA presents a good correlation with the solvent vaporization enthalpy, the FAME kinematic viscosity and the binary diffusion coefficient, which are properties representative of the cohesion energy between solvent molecules. Complete solubilization is observed for DGEBA and TGPA in methyl caprylate as the solvent, and corresponds to favorable conditions of mass and momentum transport and solvent–solvent molecule interactions. The decrease of solubility rates with the methyl ester hydrocarbon chain length increment can be explained by the increase of cohesion energy between solvent molecules and the diminution of mass transport properties due to binary diffusion coefficients and solvent viscosities.

DFT calculations have shown a greater dipolar moment for TGPA than for DGEBA and some steric hindrance in the TGPA molecule, which tend to explain the higher solubility for DGEBA.

The obtained results and the properties of long-chain vegetal esters encourage further research about environmentally friendly alternative solvents.

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References

1. Grayson, M.: *Industrial Solvents*. Wiley, New York (1983)
2. Gateau, P., Van Dievoet, F., Bouillon, V., Vermeersch, G., Claude, S., Staat, F.: Environmentally friendly properties of vegetable oil methyl esters. *OCL* **12**(4), 308–313 (2005)
3. Ahluwalia, V.K., Kidwai, M.: *New Trends in Green Chemistry*. Kluwer Academic, Boston (2004)
4. Abraham, M.A., Moens, L. (eds): *Clean Solvents, Alternative Media for Chemical Reactions and Processing*. ACS Symposium Series, vol. 819. American Chemical Society, Washington (2002)
5. Beck, H.N., Mahand, R.W., Sanders, E.S.: Relative solubility of tetrachlorohexafluoro-bisphenol-A polycarbonate in various compounds. *J. Appl. Polymer Sci.* **47**, 2161–2167 (1993)
6. Archer, W.: Determination of Hansen solubility parameters for selected cellulose ether derivatives. *Ind. Eng. Chem. Res.* **30**, 2292–2298 (1991)
7. Remigy, J.C., Nakache, E., Brechot, P.D.: Computer-aided method for the determination of Hansen solubility parameters. Application to the miscibility of refrigerating lubricant and new refrigerant. *Ind. Eng. Chem. Res.* **38**, 4470–4476 (1999)
8. Barton, A.: *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*. CRC Press, Boca Raton (1991)
9. Hansen, C.M.: Three-dimensional solubility parameter-key to paint-component affinities. *J. Paint. Tech.* **39**(511), 505–514 (1967)
10. Becke, A.D.: Density-functional thermochemistry. III—The role of exact exchange. *J. Chem. Phys.* **98**, 5648–5652 (1993)
11. Lee, C., Yang, W., Parr, R.G.: Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B Condens. Mater Phys.* **37**, 785–789 (1988)
12. Dunning, T.H., Jr., Hay, P.J.: In: Schaefer, H.F. III (ed.) *Modern Theoretical Chemistry*, vol. 3(1). Plenum, New York (1976)
13. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Jr., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Zazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., Pople, J.A.: *Gaussian 03*. Gaussian Inc., Pittsburgh, Revision B.04 (2003)
14. Van Krevelen, D.W.: *Properties of Polymers*. Elsevier, Amsterdam (1990)
15. Fagerquist, C.K., Neese, R.A., Hellerstein, M.K.: Molecular ion fragmentation and its effects on mass isotope abundances of fatty acid methyl esters ionized by electron impact. *J. Am. Soc. Mass Spectrom.* **10**, 430–439 (1999)
16. Beran, J.A., Kevan, L.: Semiempirical calculation of molecular polarizabilities and diamagnetic susceptibilities of fluorocarbons, substituted fluorocarbons, ethers, esters, ketones and aldehydes. *J. Phys. Chem.* **73**, 3860–3866 (1969)
17. Beran, J.A., Kevan, L.: Molecular electron ionization cross sections at 70 eV. *J. Phys. Chem.* **73**, 3866–3876 (1969)
18. Roussis, S.G.: Relative collision cross sections of organic ions. *J. Am. Chem. Soc. Mass Spectrom.* **6**, 803–811 (1995)
19. *CRC Handbook of Chemistry and Physics*, 66th edn. CRC Press, Boca Raton (1985–1986)
20. Medina Gonzalez, Y.: PhD Thesis, Institut National Polytechnique de Toulouse (INPT), France (2006)