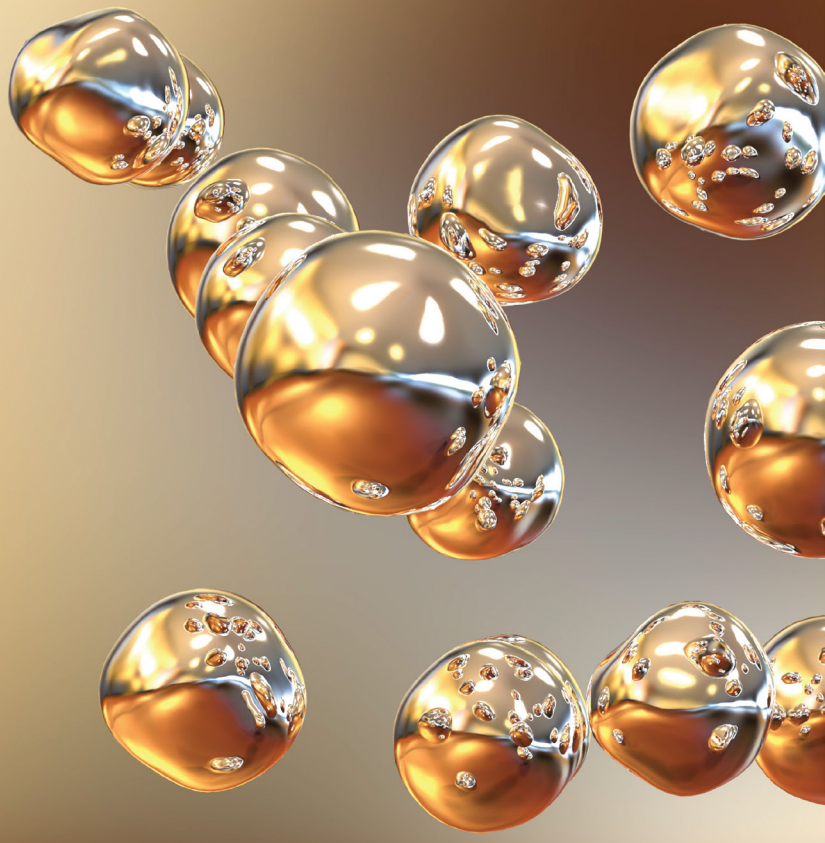
THE GREAT WORLD OF NANOTECHNOLOGY



Marcos Augusto de Lima Nobre

(Organizador)

VOL II

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PREFACE

The insertion of new and enhanced materials based on materials belonging to the Nano scale in the day-by-day has growth up in a silent way. In part, a number of works in the nanotechnology stemming of theoretical research using Density Functional Theory (DFT) and sophisticated simulation methods; another part is associated to the protected technologies associated to the military and patented nanomaterial and its process. In this sense, open access to recent aspects on the nanostructures application and properties can be reached in this book. Here, an interesting set of chapters gives opportunity of access texts that reach process and processing of nanostructures, applications of nanotechnology, advanced techniques to theoretical development. A broad set of nanostructures are here covered such as, nanocrystal, superficial nanograins, inner microstructures with nanograins, nanoaggregates, nanoshells, nanotubes, nanoflowers, nanoroad, nanosheets, Also, reveals new investigations areas as grainboundary of nanograins in ceramics and metals. A great number of software has been used as a tool of development of Science and Technologies for nanotechnology COMSOL Multiphysics 5.2. Phenomena and properties has been investigated by recent or classical techniques of materials characterization as Localized Surface Plasmon Resonance (LSPR), X-ray photoelectron spectroscopy (XPS), Field Emission Gun Scanning Electron Microscopy (FEG-SEM) with Energy Dispersive Spectroscopy (EDS), Raman Scattering Spectroscopy (RSS), X ray diffraction (XRD), ^{57}Fe Mössbauer spectroscopy, UV-vis spectroscopy, dynamic light scattering (DLS), Atomic Force Microscopy (AFM), and Field Emission Gun Scanning Electron Microscopy (FEG-SEM). In this sense, collections of spectra from Mössbauer spectroscopy, UV-vis spectroscopy and Infrared spectroscopy can be found. As a matter of fact, some chapter's item can be seemed as specific protocols for synthesis, preparations and measurements in the nanotechnology.

I hope you enjoy your reading.

Prof. Dr. Marcos Augusto Lima Nobre

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CHAPTER 12

EFFECT OF GRAPHITE NANOSTRUTURES ON THE VISCOSITY PROPERTIES OF BLENDS DIESEL-S10 AND BIODIESEL[1]

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Túlio Begena Araújo
São Paulo State University
School of Technology and Sciences – FCT/UNESP
Department of Chemistry and Biochemistry
Presidente Prudente – São Paulo
http://lattes.cnpq.br/0094407519359060

Marcos Augusto Lima Nobre
São Paulo State University
School of Technology and Sciences – FCT/UNESP
Department of Physics
Presidente Prudente – São Paulo
https://orcid.org/0000-0003-4843-3975

ABSTRACT: The nanotechnology can be applied in the changing of specific properties of functional fluids as the lubricity in fuels. In fact, nanoparticles or nanostructures can modify parameters as thermal conductivity and acting as catalyst in fuels and biofuels. The biodiesel has been added to the diesel for the decreasing of the sulfur emission. Furthermore, the lubricity is also decreased. In this sense, the desulfurization process removes molecules containing sulfur of diesel. However, both desulfurization and biodiesel addition can change the composition and diesel properties. A natural expectative is that the addition of graphite to a diesel/biodiesel composition the lubricity can be retrieved. Taking in account, diesel S10 and biodiesel, propriety can be changed via addition of graphite containing nanostructures. The viscosity of blends diesel S10/biodiesel/graphite is analyzed from rheological characterization.
KEYWORDS: Graphite nanostructures. Biodiesel. Diesel. Blends. Viscosity.

1 INTRODUCTION

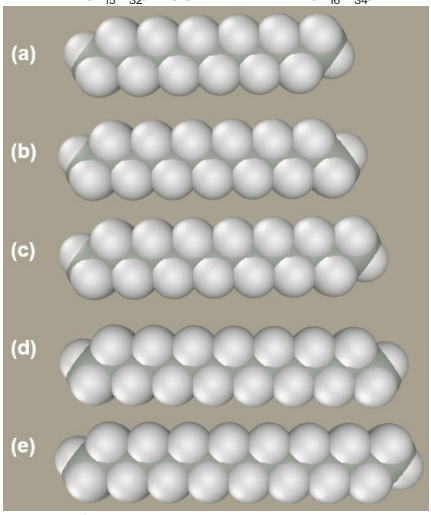
Nanotechnology involving particles at the nanoscale can be used in advanced technologies for the development of mixtures of fossil fuel and biofuel. In fact, a nanoparticle can be defined as a particle that has any of its dimensions on a nanoscale, between 1 and 100 nm. Diluting nanoparticles in a liquid, a dispersion known in modern literature as nanofluids is obtained. Several properties of liquids can be modified, and improved, with the use of nanotechnology, such as the properties thermal conductivity and diffusivity, viscosity and lubricity. All of these properties are important when working with fuel mixtures, making it possible to increase the quality of combustion

[1] This chapter is the translation of the chapter published in the book: The great world of nanotechnology / Organizer Marcos Augusto Lima Nobre. – Curitiba, PR: Artemis, 2020, Cap. 5, p. 48.

and mass and heat transport through combustion systems. Some key factors influence the application of nanofluids and should be described in detail. Among them are: size of the nanoparticles and their shapes, their composition, agglomeration, work temperature, use of surfactants and interactions at the solid-liquid interface. Fluid viscosity should be studied in conjunction with other rheological parameters. Rheology is an area of knowledge positioned between physics and chemistry. The etymology of that word has a Greek origin, specifically in the word *rheo*, which means to flow. The flow of a liquid compound is connected to the laws of physics (classical mechanics, thermodynamics, etc.) and to chemical parameters (molecular mass, molecular interactions based on secondary chemical bonds, etc.). Besides the flow of liquids, rheology comprises the deformation of solids.

In some cases, the separation between liquid and solid behaviors is not so simple. For example, when analyzing very viscous liquids, they end up behaving like solids, or in the case of solids that flow when subjected to a high enough shear stress. Many other fields of study depend directly on rheological studies for their development. Among them we have: lubricants, paints, mineral dispersions, body fluids, cosmetics, food, glass, polymer solutions, detergents, papers, among others. The importance of these studies ranges from the production and transport of the reagents to the final qualities of the product. Complex multiphase systems are part of the aforementioned applications, such as suspensions and emulsions. Considering a fossil fuel, diesel stands out as a global energy source. Despite the complex composition, which depends on its refinement process, desulphurization and the oil used, on average, has 75% saturated hydrocarbons and 25% aromatic hydrocarbons. The five predominant components in diesel are shown in Figure 1. Most diesel molecules have linear carbon chains, consisting of 12 to 16 carbons.

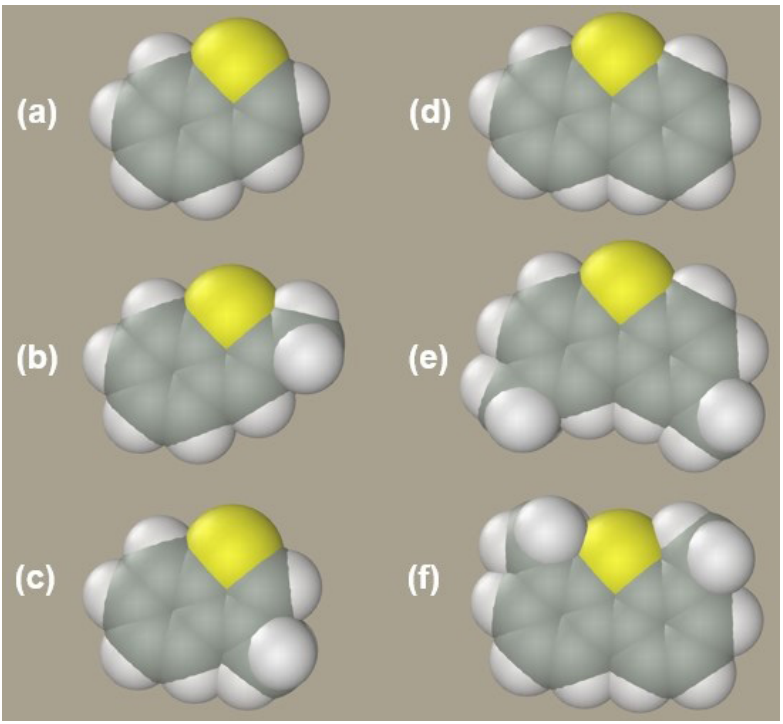
Figura 1 - Molecules of the five most abundant components in diesel: (a) dodecane ($C_{12}H_{26}$), (b) tridecane ($C_{13}H_{28}$), (c) tetradecane ($C_{14}H_{30}$), (d) pentadecane ($C_{15}H_{32}$) e (e) hexadecane ($C_{16}H_{34}$).



Source: designed by the author.

The preponderance of saturated hydrocarbons is accentuated by the desulfurization process. This process works to reduce the amount of sulfur compounds in the fuel. However, there are some deleterious effects such as the reduction of aromatic compounds and reduction of diesel lubricity. The sulfur molecules present in diesel are benzothiophenes, dibenzothiophenes and their derivatives. The molecules representing these groups are shown in Figure 2.

Figure 2 - Molecules of the main sulfur compounds of diesel: (a) benzotiofeno (C_8H_6S), (b) 2-metilbenzotiofeno (C_9H_8S), (c) 3-metilbenzotiofeno (C_9H_8S), (d) dibenzotiofeno ($C_{12}H_8S$), (e) 2,8-dimetildibenzotiofeno ($C_{12}H_{12}S$), e (f) 4,6-dimetildibenzotiofeno ($C_{12}H_{12}S$).

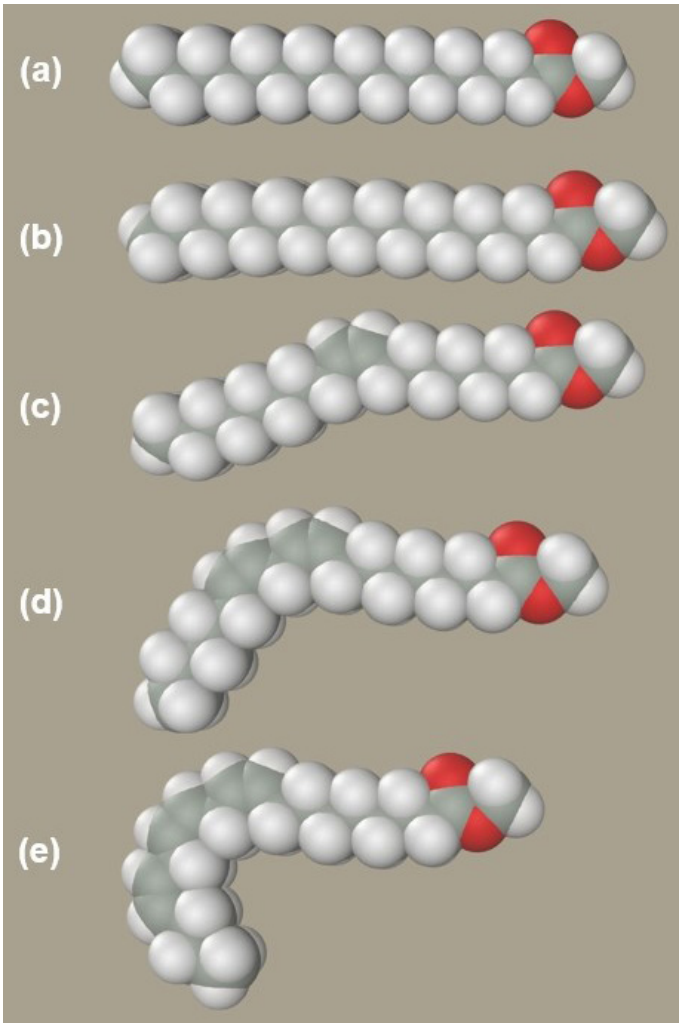


Fonte: designed by the author.

Biodiesel is produced from the transesterification of oils and fats, being composed of long chain esters, methyl or ethyl, derived from fatty acids. In Brazil, most of the biodiesel produced is derived from the transesterification of soy oil with methanol. This fuel is sold already added to the diesel.

The predominant components in biodiesel produced by methyl route are shown in Figure 3. Biodiesel molecules are, in general, larger than diesel molecules. Another important difference is that, for soy biodiesel, approximately half of its molecules are from unsaturated chains. These unsaturations cause the molecules to be non-linear, as one can see in Figure 3. In addition, one end of the ester molecules is polar, due to the bonds between carbon and oxygen atoms.

Figure 3 - Molecules of the five most abundant components in methyl soy biodiesel: (a) methyl palmitate ($C_{17}H_{34}O_2$), (b) methyl stearate ($C_{19}H_{38}O_2$), (c) methyl oleate ($C_{19}H_{36}O_2$), (d) methyl linoleate ($C_{19}H_{34}O_2$) e (e) methyl linolenate ($C_{19}H3_2O_2$).



Fonte: designed by the author.

The effects of different proportions of nanostructured graphite particles on the viscosity of mixtures of complex fluids formed by the mixture of diesel S10 and biodiesel are discussed.

2 ANALYSIS OF VISCOSITY BY RHEOLOGY OF FLUIDS

The first rheological parameter to be defined in the study of fluids is viscosity. Viscosity is the resistance to the flow of a fluid derived from the internal friction of one

part of the fluid moving to another. Starting from Newton's proposal, it is possible to write Equation 1.

$$\tau = \eta\gamma \ (1)$$

where τ is the shear stress, γ is the shear rate and η is the proportionality constant, denominated dynamic viscosity or viscosity. Not all fluids exhibit the behavior described by Eq. 1. Those that comply with Eq. 1 are called Newtonian fluids. Other fluids are non-Newtonian as they do not flow until a certain shear stress value is reached, known as yield stress. A fluid that behaves like Newtonian after the application of a minimum shear stress is denominated Bingham's plastic fluid. Equation 2 represents this behavior.

$$\tau = \tau_0 + \eta_p\gamma \ (2)$$

where η_p is the plastic viscosity and τ_0 is the yield shear stress. Both types of fluids, Newtonian and Bingham plastics have constant viscosity values as a function of the shear rate. The Ostwald-De Waele (Equation 3) and Herchel-Bukley (Equation 4) models represent fluids in which the viscosity varies as a function of the shear rate.

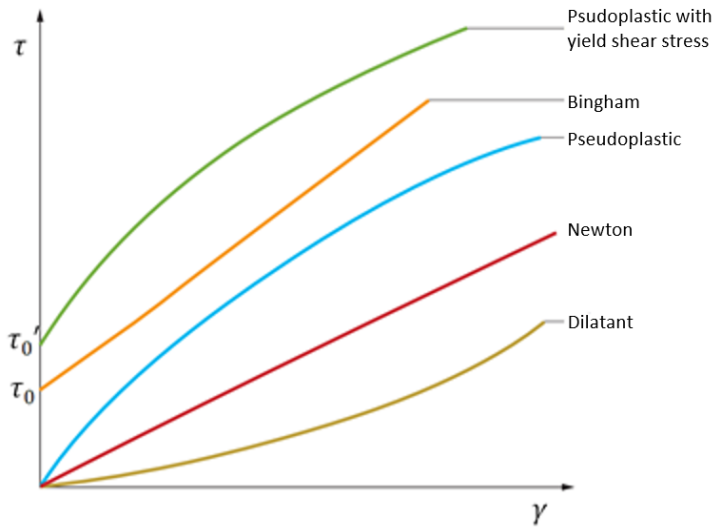
$$\tau = K\gamma^n \ (3)$$

$$\tau = \tau_0 + K\gamma^n \ (4)$$

where *K* is the consistency index parameter and *n* is the flow behavior index. By Equations 3 and 4, it is noted that the Ostwald-De Waele model applies to fluids that do not need a minimum flow stress, similarly to Newtonian fluids, while the fluids that obey the Hershel-Bukley model are refer to liquids that require minimal tension, such as Bingham plastic types. The consistency index parameter is equal to the viscosity presented by the fluid subjected to a fixed shear rate, called apparent viscosity. Fluids that respect these models and have a flow behavior index less than 1 are denominated pseudoplastics and their apparent viscosities decrease with the increase in the shear rate to which they are subjected. Fluids with a flow behavior index greater than 1 are denominated dilatants, as their apparent viscosities increase with the increase in the shear rate. Figure 4 shows rheological curves typical of fluids modeled with Equations 1, 2, 3 and 4. Some fluids have a variable behavior over time. This phenomenon is known as thixotropy. Once subjected to a constant shear rate, thixotropic fluids have their viscosity decreasing as a function of time. When leaving such fluids at rest, their viscosities slowly return to the initial value, much higher than the minimum achieved with a fixed shear rate. Fluids called rheopetics have their viscosity increased, while they are subjected to a fixed value shear rate, which

is why they are also known as antithixotropic. Like thixotropic fluids, rheopetic fluids regenerate their initial viscosity values while remaining at rest. Fluids that exhibit these types of behavior are complex in terms of shaping a law of behavior.

Figure 4 - Typical fluid curves representing Newton, Bingham, Ostwald-De Waele and Hershel-Bukley models.



Source: Araújo, 2020.

3 FUNCTIONAL DISPERSIONS

Dispersion processes and rheology of liquids with dispersed particles are of great industrial interest, as for the production of paints and solid additives in fuels. In general, for diluted systems, that is, with a volume fraction of solids less than 0.01 (1%), Equation 5 (proposed by Albert Einstein) serves as a model, through which the value of the viscosity parameter can be calculated.

$$\eta_d = \eta(1 + 2{,}5\phi) \quad (5)$$

where φ represents the volumetric fraction of solids and η_d represents the viscosity of the dispersion from the viscosity η of the fluid. In the development of this model, however, the particles considered are spherical.

In more concentrated systems, interactions between particles must be taken into account. George Keith Batchelor built a model that considers such interactions, Equation 6.

$$\eta_d = \eta(1 + 2{,}5\phi + 6{,}2\phi^2) \quad (6)$$

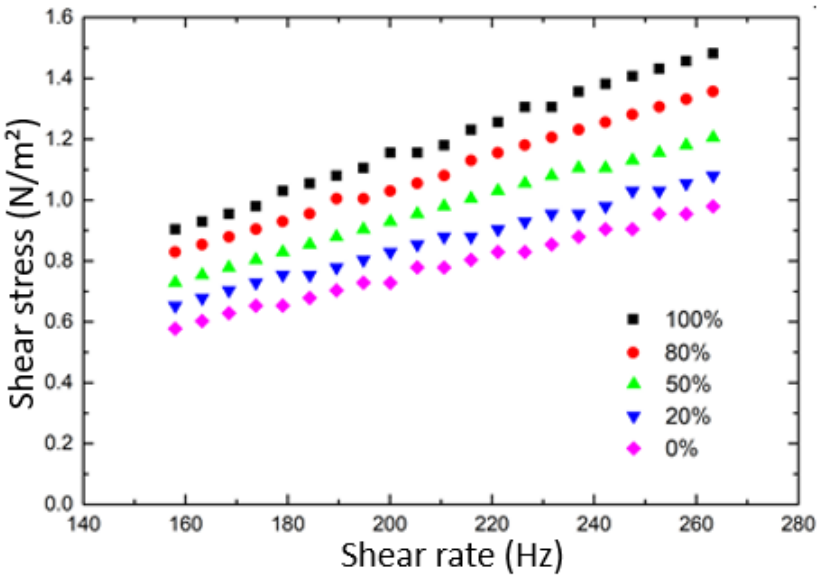
Several expressions have been proposed after Eq. 5 and 6 to describe the viscosity of dispersions. In common with each other and with Equations 5 and 6, the viscosity

parameter of a dispersion should increase with the increase in the concentration of added particles. Some studies have reported data that show results that do not fit these models.

In experiments involving complex fluids composed by blends of diesel S10 and biodiesel, with volumetric biodiesel fractions equal to 0%, 20%, 50%, 80% and 100% in the case, these show the behavior of Newtonian fluids for the shear rate range between 158 Hz and 263 Hz. This behavior is shown in Figure 5.

Figure 5 shows rheological curves, shear stress versus shear rate, for diesel S10, biodiesel and diesel S10/biodiesel blends. The shear stress varies linearly as a function of the shear rate of the blends.

Figure 5 - Shear stress versus shear rate for blends of diesel S10 and biodiesel, as a function of the volumetric fraction of biodiesel.



Source: Lanfredi, 2019.

Newtonian fluid behavior is as simple as possible for fluids. From the analysis of the behavior of the blends, it was possible to determine the values of their viscosities. These values are listed in Table 1. When adding nanostructured graphite particles to these blends, some results, even surprising, were obtained. To each of these samples, proportions of graphite powder equal to 0.2%, 0.4% and 0.8% by volume were added. All these quantities of graphite represent volumetric fractions suitable for the model proposed by Einstein. In the same experimental conditions, the dispersions maintained the behavior of Newtonian fluids, as can be seen in Figure 6. The results obtained for the viscosity values of all these samples are listed in Table 1.

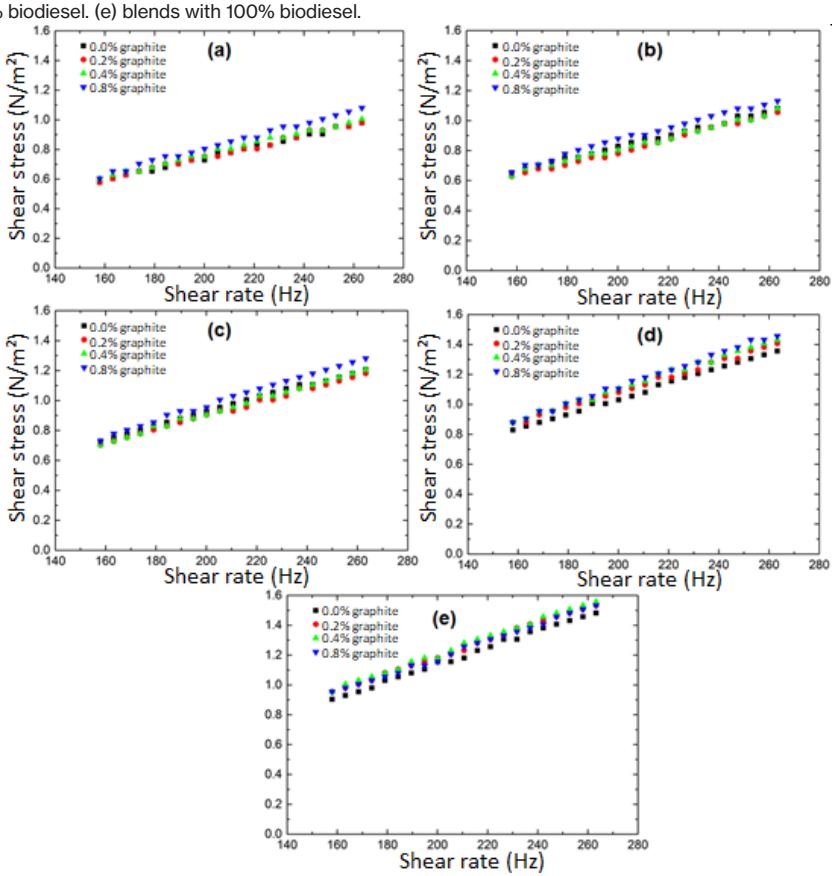
Table 1 - Viscosities in mPa.s of the binary blends of diesel S10 and biodiesel, with addition of graphite particles, at 293.15 K.

Volumetric fraction of biodiesel (%)	Volumetric fraction of graphite (%)			
	0.0	0.2	0.4	0.8
0	3.70±0.04	3.73±0.05	3.82±0.04	4.03±0.07
20	4.12±0.05	3.97±0.05	4.05±0.06	4.31±0.07
50	4.62±0.03	4.48±0.04	4.54±0.05	4.84±0.07
80	5.19±0.04	5.40±0.07	5.51±0.06	5.58±0.05
100	5.69±0.05	5.92±0.06	6.01±0.06	5.89±0.07

Source: Lanfredi, 2019.

According to the data listed in Table 1, some dispersions had lower viscosity values than solids-free fluids. This phenomenon occurs in four samples, those containing volumetric fraction of biodiesel equal to 20% and 50% and volumetric fraction of graphite equal to 0.2% and 0.4%. These results appear to conflict with Equation 5. However, graphite particles, due to their molecular structure, tend to have flattened structures, such as layers or sheets.

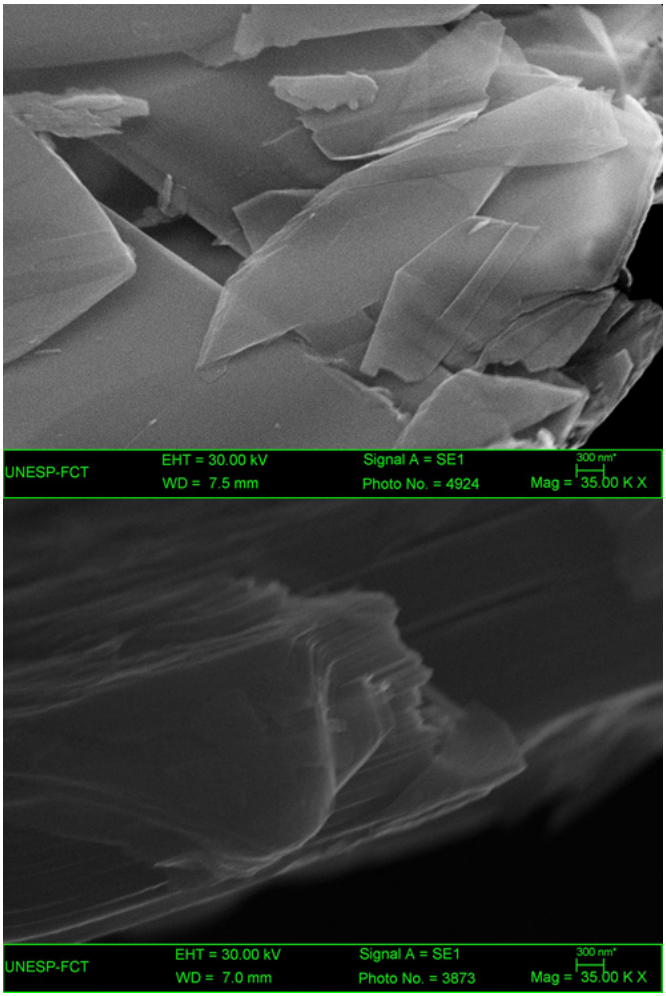
Figure 6 - Shear stress versus shear rate for blends of diesel S10 and biodiesel, as a function of the volume fraction of graphite. (a) blends with 0% biodiesel. (b) blends with 20% biodiesel. (c) blends with 50% biodiesel. (d) blends with 80% biodiesel. (e) blends with 100% biodiesel.



Souce: Lanfredi, 2019.

Figure 7 shows micrographs of the graphite powder, obtained by scanning electron microscopy, in which it is possible to observe the nanostructures of the graphite particles. Thin blades can be identified with a 35000-fold magnification. In the upper image, extensive layers are identified with tenths of thickness of the size bar, 300 nm. In the bottom image of Fig. 7, an edge shows unequivocally that nanometric layers overlap.

Figure 7 - Micrographs of the graphite powder. 35000 times magnification.



Source: author.

According to scanning electron microscopy (SEM) micrographs, these graphite particles are composed of a nanostructure, composed of laminar structures of nanometric thickness. The model of action on the viscosity of the blends is not evident, but one idea is that the nanostructures of blades induce some type of lamellar order in the suspension. Thus, hypothetically, after the ordering of the system subjected to shear rates in a unidirectional way, there is a decrease in the viscosity of the analyzed complex fluids.

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ABOUT THE ORGANIZER

MARCOS AUGUSTO DE LIMA NOBRE: Assistant Professor and Researcher (2006 - present), with citation name M. A. L. Nobre, at the São Paulo State University (UNESP), School of Science and Technology, Department of Physics, campus at Presidente Prudente-SP. Head and Founder (2002) of the Laboratory of Functional Composites and Ceramics (LaCCeF acronym in Portuguese, the native idiom), Lab certified by PROPE-UNESP/National Council for Scientific and Technological Development/CNPq*. Grants from National Council for Scientific and Technological Development (CNPq), 2020-2023, 2019-2021 and 2010-2012. Granted with Young-Researcher scholarship by the São Paulo Research Foundation, FAPESP (São Paulo, São Paulo) (2002 - Summer of 2005). Postdoctoral fellow at the Polytechnic School of the University of Sao Paulo (POLI USP-SP) Metallurgy and Materials Science Department with FAPESP Scholarship (1999-summer of 2000). PhD in Science, CAPES Scholarship (Physical Chemistry 1999) by the Chemistry Department, UFSCar-SP. Master in Chemistry CNPq scholarship (Physical Chemistry 1995) by the Chemistry Department, UFSCar-SP. Licentiate degree (4-year of study) in Physics (1993) CNPq and CNPq-Rhae scholarships by the Physics Department, UFSCar-SP. Associate Editor of the Micro & Nano Letters - IET 2019-2020. Associate Editor of the Micro & Nano Letters-Wiley, 2020 - present. Ethycal Editor of the Applied Mathematics Science (Reuse) m-Hikari and Modern Research in Catalysis, Irvine-CA, USA (2017- date). Editorial board member of the Artemis Editora, Brazil. Nowadays, have 02 patents. Has published 80 papers at 39 different indexed Journals of renowned Editors. In May/25/2021, has been cited 1379 times, at 76 papers (47 with citations), in according to the ResearchID actual Publons base having an H-index equal to 23. Academic Google score: H = 28, i10 = 45 and 2338 citations. Reviewer of more than three dozen of journals. Have more than 580 communications and presentation in National and International Congress and Symposiums, from these 150 has been published as Conference Paper. Author or co-author of 20 Chapters of book approaching Scientific Divulgation, Teaching of Physic and Chemistry for teachers actuating in the graduating degree. For this, the Nanoscience and Nanotechnology have been the first strategy. Received tens of National and International Awards, Honorable mentions and distinction mentions, as well as titles. Research skills: Materials Science, Advanced Ceramic Processing, Linear and Non-linear Advanced Dielectrics Materials, Solid state chemistry, Impedance spectroscopy of solids and fluids, Structural Characterization via Mid infrared Spectroscopy with Fast-Fourier-Transformed of solid and fluids, Structural and non-structural Phase Transitions in Semiconductor Ferroelectrics. Also, Molecular Interactions in Functional Fluids as biofuels and its blends, probed via mid infrared Spectroscopy. Research interests: New Functional Materials as

amorphous composite based on carbon/nanoparticles and Semiconductor Ferroelectrics. Member of the Program of Post-Graduation in Chemistry at UNESP - Campus of São José do Rio Preto, IBILCE UNESP – SP, Brazil.

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