Deep Eutectic Solvents as a Green Alternative for Multilayer Graphene Production

***Flávia Monique Bispo Vieira[1], Halana Santos Lisboa[1], Paulo de Morais[3,4], Fermin Fidel Herrera Aragón[4], Luiz Fernando Romanholo Ferreira[3], Ranyere Lucena de Souza[1,2]**

[1] Universidade Tiradentes, Aracaju-SE, Brazil
[2] Instituto de Tecnologia e Pesquisa, Aracaju-SE, Brazil
[3] Universidade Católica de Brasília, Brasília-DF, Brazil
[4] Universidade de Brasília, Brasília-DF, Brazil
Universidade Tiradentes, Aracaju - SE, Brazil; flavia.mvieira@souunit.com.br

Abstract: Graphene has remarkable physical and chemical properties that make it highly attractive for a wide range of technological applications, including electronic devices, advanced composite materials, and energy storage and conversion systems. Among its main characteristics are high electronic mobility, high thermal conductivity, and mechanical strength superior to that of steel. However, the controlled, environmentally sustainable, and economically viable production of graphene on an industrial scale still represents a scientific and technological challenge. In this context, shear-assisted liquid exfoliation emerges as a promising alternative, especially when associated with green and renewable solvents. Deep eutectic solvents stand out for being biodegradable, low cost, non-volatile, safe to handle, and easy to prepare, in addition to allowing the modulation of their physicochemical properties according to the selected donor-acceptor pair. This study aimed to evaluate the production of multilayer graphene from liquid exfoliation by intense shear, using DES as a dispersing medium. Two formulations were analyzed: choline chloride with levulinic acid (ChCl:Lev) and with lactic acid (ChCl:Lac), both in a 1:2 molar ratio. The samples were stirred at 7500 rpm for 80 minutes. Characterization was performed by Raman and FTIR spectroscopy. The ChCl:Lev system had an I_2D/I_G ratio of 0.62 and a Full Width at Half Maximum (FWHM) of 39.83 cm^{-1}, suggesting graphene with 3 to 5 layers. The ChCl:Lac system exhibited an FWHM of 26.70 cm^{-1}, indicating thicker structures. The results confirm the effectiveness of DES in the production of multilayer graphene, with emphasis on the ChCl:Lev system, which favored the obtaining of thinner and potentially more functional sheets for high-performance applications.
Keywords: DES. Graphene. Liquid exfoliation.
Abbreviations: ChCl:Lev, Choline Chloride: Levulinic Acid. ChCl:Lac, Choline Chloride: Lactic Acid. FTIR, Fourier transform infrared spectroscopy. FWHM, Full Width at Half Maximum.

1. Introduction

The development of advanced materials that combine low environmental impact with high performance has been driven by the growing search for sustainable technologies. Graphene is an allotrope of carbon with a two-dimensional hexagonal structure, composed of one or a few layers of carbon atoms arranged in a honeycomb-like network. It has an electrical conductivity of around 10^6 $S \cdot m^{-1}$, a thermal conductivity of around 5000 $W \cdot m^{-1} \cdot K^{-1}$, an elastic modulus of approximately 1 TPa, and a mechanical strength of around 130 GPa. In addition, it has an optical transmittance of about 97.7% in the visible spectrum, which enables its application in electronic devices, transparent coatings, functional composites, and energy conversion and storage systems [1-2].

Even with different graphene production routes, producing it on a large scale is still a challenge. Among these routes, liquid phase exfoliation (LPE) emerges as a promising technique [3], but it is commonly performed with organic solvents such as N-methylpyrrolidone (NMP) and dimethylformamide (DMF), which, although

effective, have a high environmental impact and high toxicity [4-5].

Considering the search for more sustainable chemical solutions, deep eutectic solvents (DES) emerge as viable alternatives. Consisting of a hydrogen bond donor and acceptor, DES offers advantages such as low cost, low toxicity, biodegradability, and reduced flammability [6]. In addition, they offer the possibility of modulating properties such as viscosity and surface tension, the latter being, when close to that of graphene (~40 mN/m), a critical parameter for successful exfoliation [7].

Thus, this work aims to produce graphene multilayers through high shear exfoliation, using deep eutectic solvents formulated from choline chloride in combination with lactic and levulinic acids. It also seeks to evaluate the physicochemical properties of these solvents and their efficiency as sustainable means for the dispersion and exfoliation of graphite.

2. Methodology

2.1. Preparation of Deep Eutectic Solvents (DES)

Deep eutectic solvents (DES) were prepared using choline chloride (ChCl) as the hydrogen bond acceptor and lactic or levulinic acids as donors. The mixtures were formulated at a 1:2 molar ratio (ChCl:acid), followed by moderate magnetic stirring at 80°C until complete visual homogenization of the system, indicating the formation of the eutectic solvent. After preparation, the DES were stored in amber bottles, under a hermetic seal, to prevent moisture absorption and degradation by exposure to light.

2.2. Physical-chemical and structural characterization of DES

To determine the density and viscosity of the solvents, an SVM 3000 automatic viscometer (Anton Paar, Austria) was used, operating at 25 °C. Surface tension was measured using the hanging drop method with a tensiometer (Lauda Scientific, Germany), also at a temperature of 25 °C. The chemical interactions and functional groups present in the systems were identified using Fourier transform infrared spectroscopy (FTIR), using a Cary 630 spectrometer (Agilent Technologies, Germany), equipped with an attenuated total reflectance (ATR) accessory. The analyses were performed in triplicate, in the spectral range from 4000 to 600 cm^{-1}, with a resolution of 4 cm^{-1}.

2.3. Graphene production by high shear exfoliation (LPE)

Graphite exfoliation was conducted using a high shear mixer, model L5M-A (Silverson Machines, UK). In each test, 2.5 g of natural graphite was dispersed in 50 mL of the respective DES in a 100 mL beaker. The mixture was stirred at 7500 rpm for 80 minutes [8-9].

For thermal control, the beaker was kept immersed in an ice bath throughout the process. After exfoliation, the resulting suspension was centrifuged at 3000 rpm for 40 minutes. The decanted material was then subjected to vacuum filtration, and the retained solid was dried in an oven at 80 °C until all DES residues were eliminated.

2.4. Characterization of graphene by Raman spectroscopy

The structural characterization of graphene was performed by Raman spectroscopy at room temperature using a Horiba LabRAM HR Evolution spectrometer equipped with a 532 nm laser. The spectra were acquired in the range of 1000 to 3000 cm^{-1}, with an average of three scans per analysis point. Data processing was performed using OriginPro® 2018 software, including baseline correction and spectrum normalization. The 2D band was deconvoluted by fitting Gaussian and Bigaussian peaks, allowing the number of graphene layers to be estimated based on the bandwidth (FWHM) and the ratio between the intensities of the I_2D/I_G bands.

3. Results

3.1. Physical-chemical characterization of DES

Table 1 lists the physical and chemical properties of deep eutectic solvents (DES), such as density, viscosity, and surface tension.

Table: Physical-chemical characterization of Lactic Acid (ChCl: Lac) and Levulinic Acid (ChCl: Lev) DES.

DES	ChCl: Lac	ChCl: Lev
Surface tension (mN/m)	36,73	41,17
Density (g/cm^3)	1,1724	1,1368
Viscosity (m^2/s)	0,0643	0,0868

The physical and chemical properties of DES prepared with choline chloride and organic acids vary depending on the nature of the hydrogen donor. The ChCl:Lev system showed higher surface tension (41.17 mN/m) and viscosity (0.0868 m^2/s), as well as lower density (1.1368 g/cm^3), compared to the ChCl:Lac system, whose values were 36.73 mN/m, 0.0643 m^2/s, and 1.1724 g/cm^3, respectively. These differences can influence solvent-material interactions during the exfoliation process, since parameters such as surface tension and viscosity affect the shear regime, dispersion stability, and penetration into the graphite layers.

3. 2. Chemical characterization by FTIR

FTIR spectroscopy was used to investigate the formation and molecular interactions of DES. Figures 1 and 2 show the absorption spectra of pure choline chloride and the ChCl:Levulinic and ChCl:Lactic systems.

Figure 1. FTIR spectroscopy of the eutectic solvent of ChCl and levulinic acid and its individual components.

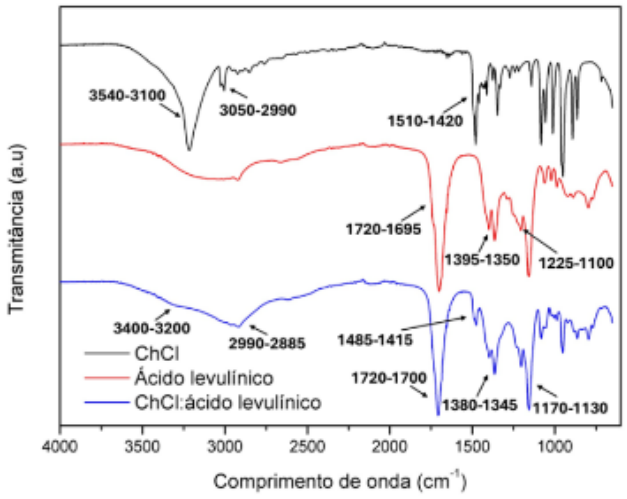
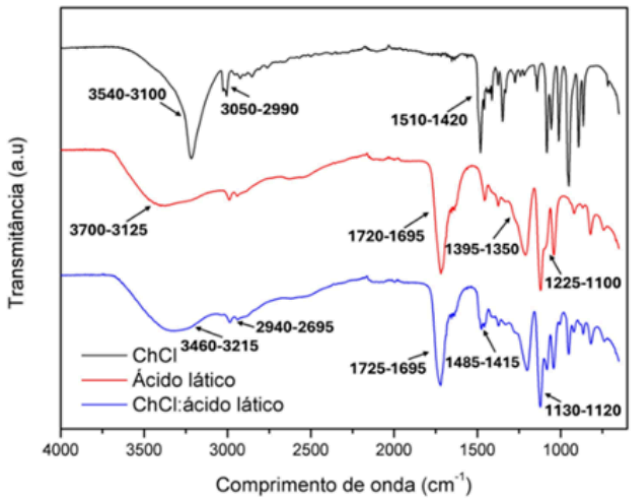


Figure 2. FTIR spectroscopy of the eutectic solvent of ChCl and lactic acid and its components.



The shift of the bands associated with hydroxyl (–OH) to the range of 3400–3200 cm^{-1}, and of carbonyl (C=O) to 1720–1700 cm^{-1}, indicates the presence of strong intermolecular interactions, especially hydrogen bonds [10]. The formation of a network of interactions characteristic of a deep eutectic solvent (DES) is further reinforced by the presence of new bands in the regions of 1485–1415, 1380–1345, and 1170–1130 cm^{-1} [11]. In the ChCl:lactic acid system, similar effects are observed, with displacement of the –OH band to the range of 3460–3215 cm^{-1} [12], in addition to additional bands attributed to reorganized C–O bonds, also compatible with the formation of hydrogen bonds. These spectral shifts and reorganizations highlight the effective formation of DES, promoted by specific interactions between its components [13].

3.3. Production of Graphene Multilayers

Table 2 shows the production of graphene multilayers obtained with the two solvent systems.

Table 2: Graphene production obtained by exfoliation in DES in 80 minutes of exfoliation.

DES	Multilayer graphene (mg)
ChCl: Lactic acid	44,00
ChCl: Levulinic acid	69,5

The production of multilayer graphene was influenced by the physicochemical properties of the deep eutectic solvents (DES) used. The ChCl:levulinic acid system showed a higher yield (69.5 mg) compared to the ChCl:lactic acid system (44.0 mg). This difference may be related to the greater similarity between the surface tension of graphene (~40 mN/m) and

that of ChCl:Lev (41.17 mN/m), which may favor interfacial interaction between the solvent and the graphitic layers, promoting greater efficiency in the exfoliation process [14]. Furthermore, although it has higher viscosity (0.0868 m²/s), ChCl:Lev may have provided a more effective shear regime for graphene dispersion, possibly due to a more favorable balance between solvation forces and colloidal stability. Thus, the results suggest that the combination of these physicochemical properties contributed to the greater layer separation capacity observed with levulinic acid.

3.4. Raman characterization of graphene produced

Figures 3 and 4 show the Raman spectra of the graphene produced. Both graphene exfoliation systems with DES show a G band at ~1590 cm^{-1} and a 2D band at ~2725 cm^{-1}.

Figure 3. Raman spectra of graphene obtained using the ChCl:lactic acid (G@ChCl:Lac) and ChCl:levulinic acid (G@ChCl:Lev) systems, highlighting the G band (~1590 cm^{-1}), characteristic of in-plane vibrations of the graphitic lattice.

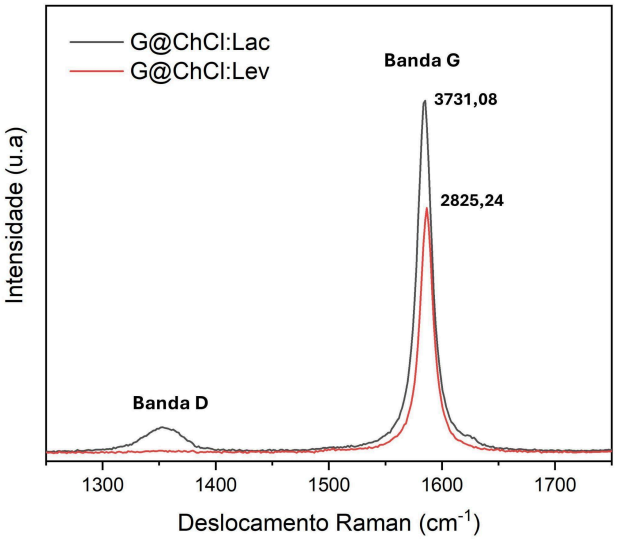
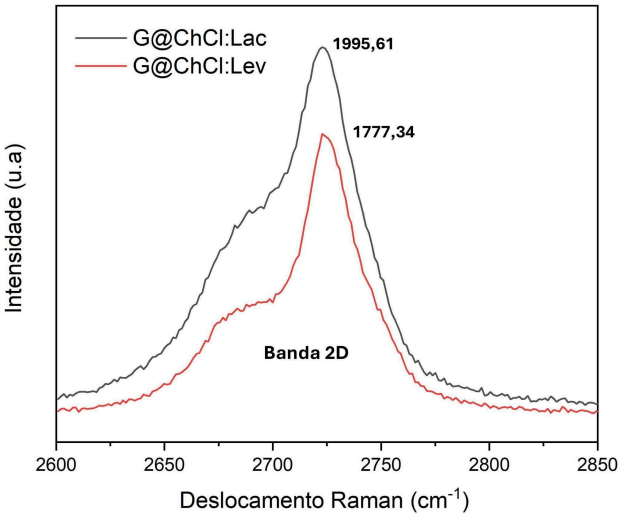


Figure 4. Raman spectra of graphene obtained using the ChCl:lactic acid (G@ChCl:Lac, black) and ChCl:levulinic acid (G@ChCl:Lev, red) systems, highlighting the 2D band (~2700 cm^{-1}), which corresponds to the second-order double-resonance mode and is commonly used to estimate the number of graphene layers.



The Raman spectra after 80 minutes of exfoliation with the ChCl:Lac and ChCl:Lev systems revealed differences in the G (~1590 cm^{-1}) and D (~1350 cm^{-1}) bands. The G band showed greater intensity in the ChCl:Lac system (3731.08 u.a.) than in the ChCl:Lev system

(2825.24 u.a.), indicating possible greater structural ordering in the latter. The D band was observed only in the spectrum of the ChCl:Lac system, suggesting the presence of structural defects resulting from the exfoliation process.

Analysis of the 2D band revealed an FWHM of 39.83 cm^{-1} for the ChCl:Lev system and 26.70 cm^{-1} for the ChCl:Lac system, as observed in the spectra obtained. The I_2D/IG ratios, calculated from the maximum intensities of the 2D (1777.34 and 1995.61) and G (2825.24 and 3731.08) bands, were 0.62 and 0.53, respectively. According to Karamat et al. (2016) [15], I_2D/IG ratios lower than 1, associated with FWHM values between 30 and 60 cm^{-1}, are indicative of the presence of multilayer graphene, especially with three to five layers. In this context, only the G@ChCl:Lev system meets these spectral criteria, being compatible with the formation of graphene with up to five layers.

In contrast, the G@ChCl:Lac system, with an FWHM of less than 30 cm^{-1}, suggests a distinct structure, possibly related to the presence of graphene with more than six layers. This interpretation is corroborated by Nuayi et al. (2024) [16] and Kumar et al. (2021) [17], who associate reduced FWHM values with systems with a greater number of layers obtained by liquid exfoliation.

5. Conclusion

The results confirm the feasibility of using deep eutectic solvents (DES) for the production of multilayer graphene via high-shear exfoliation. Among the systems evaluated, the DES composed of choline chloride and levulinic acid exhibited the most consistent performance, with an I_2D/I_G ratio of 0.62 and a FWHM of 39.83 cm^{-1}, both consistent with the presence of graphene containing 3 to 5 layers. In contrast, the lactic acid-based system showed a FWHM of 26.70 cm^{-1}, suggesting the possible formation of structures with more than six layers. The Raman spectra support the effectiveness of the exfoliation process in DES and highlight its potential as a sustainable route for obtaining carbon-based nanomaterials.

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