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# Tribological properties of Sargassum carbon dots as additives in water-based lubricants

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## ABSTRACT

This study evaluated the tribological characteristics of a novel eco-friendly water-based lubricant containing carbon dots (CDs) obtained from Sargassum as additives. The mean friction coefficient of a lubricant containing 5 mg/ml CD contents was 78 % lower than that of pure water. Furthermore, a correlation between wear rate, contact shape, and kinetic vertical ball displacement was also established.

## 1. Introduction

Metalworking processes induce high friction, high temperature, and wear which can be reduced by water-based lubricants [1]. It is well known that water is a poor lubricant, the use of carbon dots (CDs) as additives significantly improves the lubricating properties of water [2–4]. Over the last decade, numerous organic [5,6] and green biomass [7–9] precursors have been used to produce such nanometric particles. Seaweeds like Sargassum Fluitans are abundant free natural carbon resources used in the preparation of nitrogen and sulfur co-doped CDs (N, S-CDs) [10,11]. A lubricant containing pure water as a base and CDs obtained from Sargassum as additives was characterized in this study. To our knowledge, the excellent load-dependent friction reduction properties in boundary lubrication regime were better than those obtained in previous studies dealing with pure water-based lubricants. [12–14]. Moreover, the anti-wear performance, evaluated with the wear rate parameter and a new measure of the kinetics of vertical ball displacement, increased with load.

## 2. Experimental section

Sargassum seaweeds were collected at 16.01° N 61.55° W along the coast of Guadeloupe (French West Indies) in March 2021. The samples were rinsed, dried, and then ground before being refluxed during 30 min.

The size of the CDs was evaluated by atomic force microscopy (AFM) (Nano-Observer, Scientec). Their structure was characterized by

Fourier-transform infrared spectroscopy (FTIR) (PerkinElmer) and Raman spectroscopy (HR evolution Horiba). The UV–vis and Fluorescence spectra of CDs suspension were recorded on PerkinElma Lambda and XLSPERkinElma FL 6500 respectively. Tribological experiments were performed in air (relative humidity:  $80 \pm 5\%$ ) with a home-built alternative ball-on plane tribometer equipped with an interferometric system from SmartAct which allows the measurement of the vertical displacement of the ball during the friction tests. A 316L rolling steel ball and plane were used during this procedure. The sliding speed was 20 mm/s and the applied load varied from 5 N to 30 N. The wear volume was estimated by 3D profilometry (Altisurf 500).

## 3. Results and discussion

The oblong shape on topographic AFM image (Fig. 1a) is due to the AFM tip convolution and the maximum height distribution of the CDs is  $7.32 \pm 1.25$  nm.

From the FTIR spectrum (Fig. 1b), N-H and O-H stretching vibration bands are visible around  $3300\text{ cm}^{-1}$  and  $3200\text{ cm}^{-1}$ , respectively. The area between  $2900$  and  $3000\text{ cm}^{-1}$  associated with = C-H stretching is very weak, as are the peaks at  $1705\text{ cm}^{-1}$  and  $1750\text{ cm}^{-1}$  attributed to C = O stretching vibrations. The strong peak at  $1570\text{ cm}^{-1}$  could be related to N-H deformations and/or deformations of aromatic rings due to C = C elongations. The  $1410\text{ cm}^{-1}$  absorption band corresponds to O-H deformation within the C(O)O-H group and/or N-H elongation. The peak at  $1360\text{ cm}^{-1}$  is associated with C-N elongation whereas the  $1109\text{ cm}^{-1}$  and  $1129\text{ cm}^{-1}$  peaks are attributed to C-O elongation in acids and

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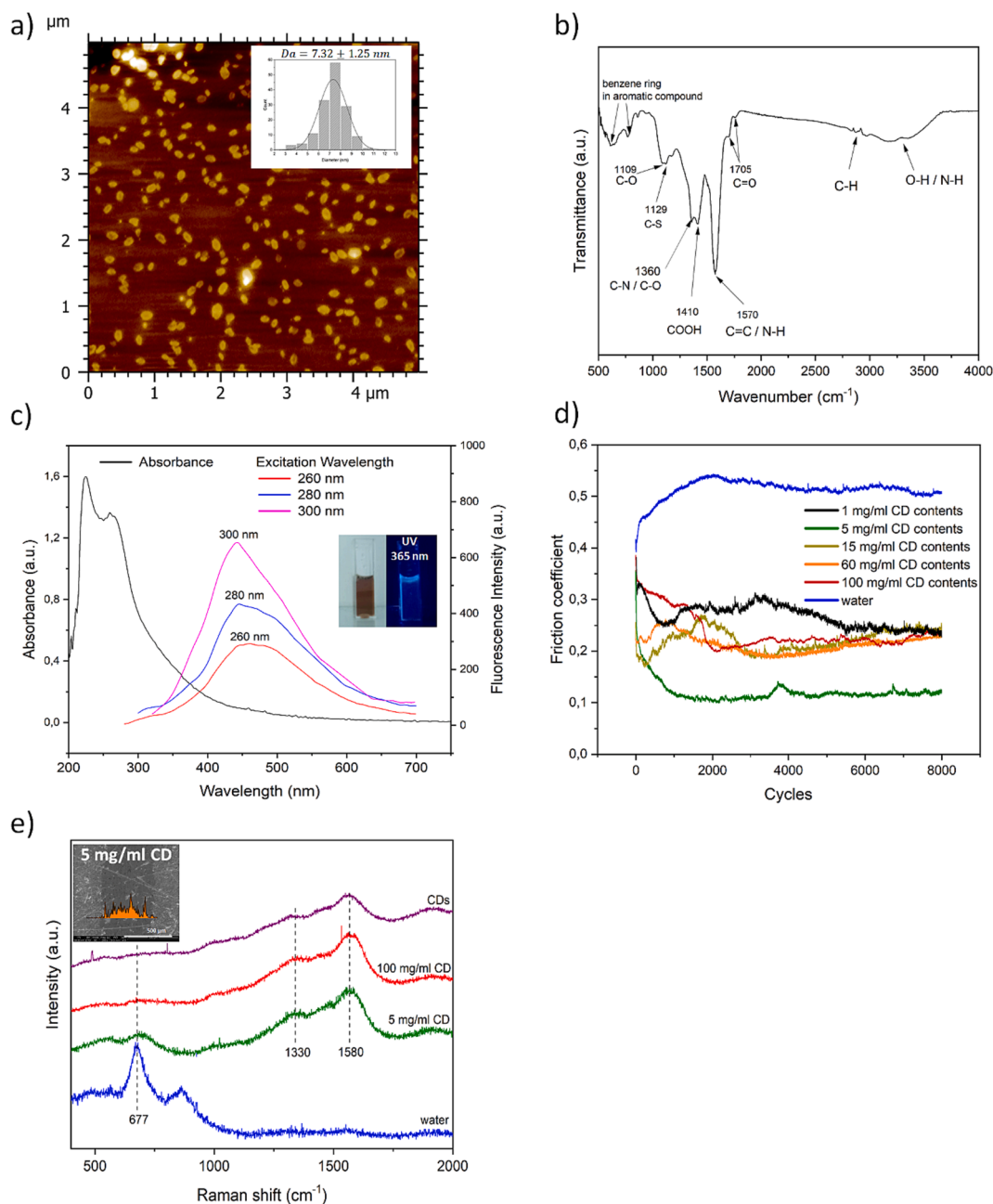
C-S elongation, respectively.

As shown in Fig. 1c aqueous suspension of CDs emits fluorescence at 443 nm under 300 nm excitation. The COF at 20 N as a function of the number of cycles (Fig. 1d) remained stable from cycle 2000 until the end. By decreasing the amount of CDs from 100 mg/ml to 5 mg/ml, the friction decreased from 0.22 to 0.12, corresponding to a diminution of 78 % of the mean COF relative to that of the pure water. These values are lower than those obtained for ammonium citrate [12], sodium citrate [13], or graphite powder [14] in deionized water. With 1 mg/ml CD contents the COF increased.

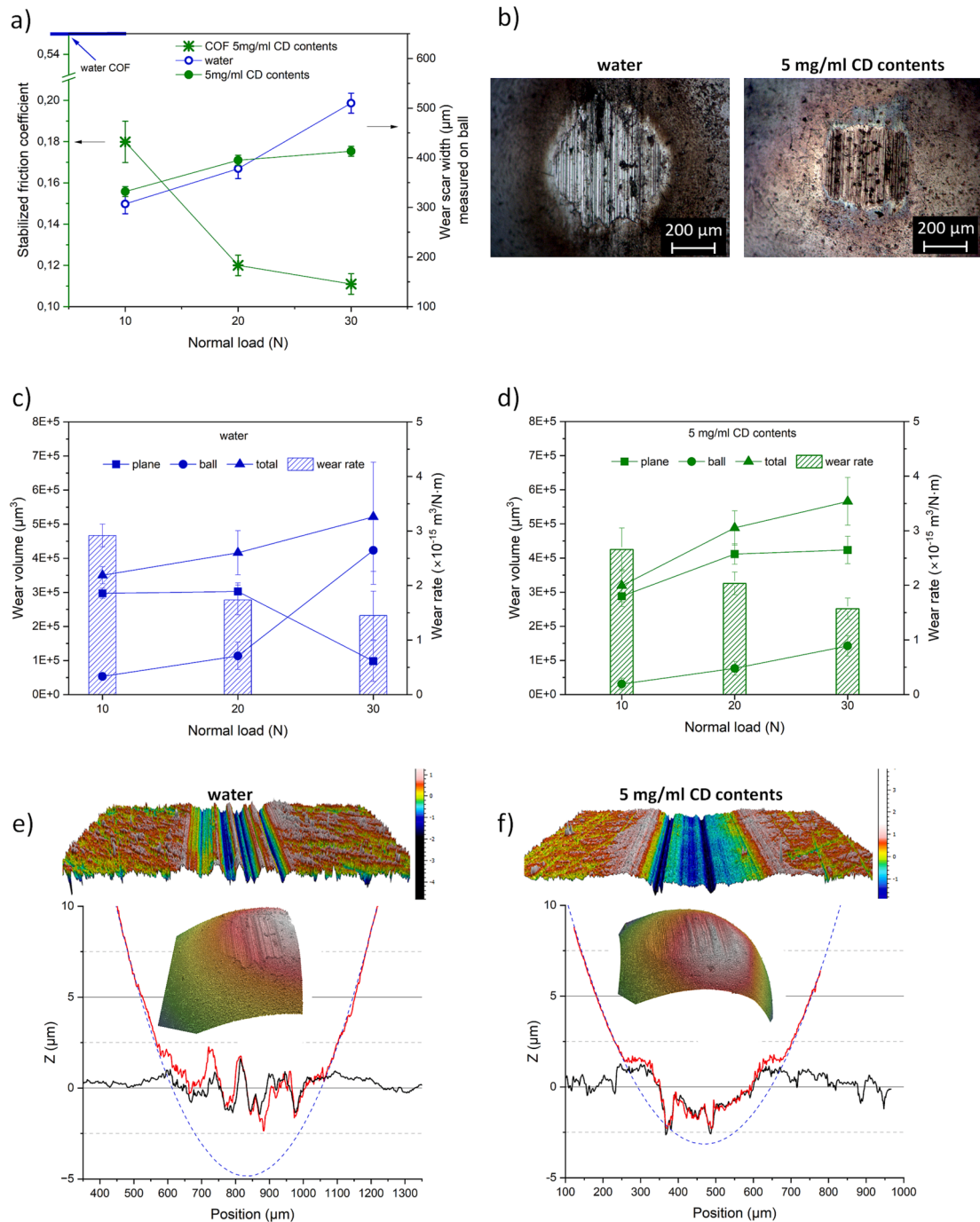
As shown in Fig. 1e, the Raman spectra corresponding to pure CDs and the 100 and 5 mg/ml tribofilms are similar, with a G peak at  $1580\text{ cm}^{-1}$ , and a D peak at  $1330\text{ cm}^{-1}$ . In the inset graph, each point corresponds to the area under the carbon peak between  $1120\text{ cm}^{-1}$  and

$1760\text{ cm}^{-1}$ , calculated on 151 spectra on a line across the wear track obtained with the 5 mg/ml CD solution. The profile reveals a homogeneous carbon film. Moreover, a weak iron oxide ( $\text{Fe}_3\text{O}_4$ ) band appears at  $670\text{ cm}^{-1}$  on the film at 5 mg/ml and cannot be distinguished at higher concentrations. In conclusion, CDs used as additives protect the steel surfaces with a thin carbon tribofilm which prevents oxidation. Metallic surfaces become positively charged during the friction process [15], polar hydroxyl and nitrogen functional groups of CDs can then adsorb to form a tribofilm, [16,17].

In order to evaluate the anti-wear properties of the CDs, tribological experiments were conducted on pure water-based lubricants with or without 5 mg/ml CDs, with applied loads of 10 N, 20 N, and 30 N; the experiments were stopped at 3000 cycles at the end of the induction period. The results are plotted in Figs. 2 and 3.



**Fig. 1.** (a,b) AFM topographic image and size distribution and FTIR spectra of the CDs; (c) UV-visible absorption and photoluminescence emission spectra of CDs in water; (d) Friction curves as a function of the cycles with CD contents (load 20 N); (e) Raman spectra as a function of CD contents. Inset: profile of carbon Raman peak intensity.



**Fig. 2.** (a) COF and wear scar width as a function of normal force; (b) Optical images of the ball scars; (c) and (d) Wear volume and wear rate as a function of normal load; (e) and (f) 3D Profilometry images at 30 N and corresponding 2D profile in the middle of the wear scar.

For water lubrication, the COF (0.55) does not vary with the normal load and, the scar width increases with normal load from 307 μm to 510 μm, maintaining a spherical shape (Fig. 2a and b). As seen in Fig. 2c the plane wear volume decreases from  $2.9 \times 10^5 \mu\text{m}^3$  to  $0.1 \times 10^5 \mu\text{m}^3$  whereas the ball wear volume increases from  $0.5 \times 10^5 \mu\text{m}^3$  to  $4.2 \times 10^5 \mu\text{m}^3$ , allowing us to determine a decrease in wear rate from  $2.9 \times 10^{-15} \text{m}^3/\text{N}\cdot\text{m}$  to  $1.45 \times 10^{-15} \text{m}^3/\text{N}\cdot\text{m}$ . The 2D profile across the middle of the wear scar (3D image) shows that the worn area of the plane exhibits grooves which evidence that the wear process is caused by plastic deformation. On the contrary, the ball is clearly damaged by the loss of material even if the surface is plastically deformed. The contact geometry clearly changes from ball-on-plane to plane-on-plane. Moreover,

Fig. 3 reveals a vertical displacement of the ball of 2.7 μm during the 200 first cycles, followed by one of only 2 μm during the remaining 2900 cycles. This last measurement associated with low wear volume of the plane suggests a quick degradation of the ball towards a plane to plane contact and then a slow wear of the ball. The modification of the contact shape explains the decrease in wear rate.

For the lubricant with 5 mg/ml CD contents in Fig. 2a, the COF decreases from 0.18 at 10 N to 0.11 at 30 N, and the width of the wear scar increases from 330 μm to 413 μm with a rectangular shape as illustrated at 30 N in Fig. 2b. The ball and plane wear volumes (Fig. 2d) increase from  $0.3 \times 10^5 \mu\text{m}^3$  to  $1.4 \times 10^5 \mu\text{m}^3$  and from  $2.9 \times 10^5 \mu\text{m}^3$  to  $4.2 \times 10^5 \mu\text{m}^3$  respectively. The wear rate decreases from  $2.65 \times 10^{-15} \text{m}^3/$

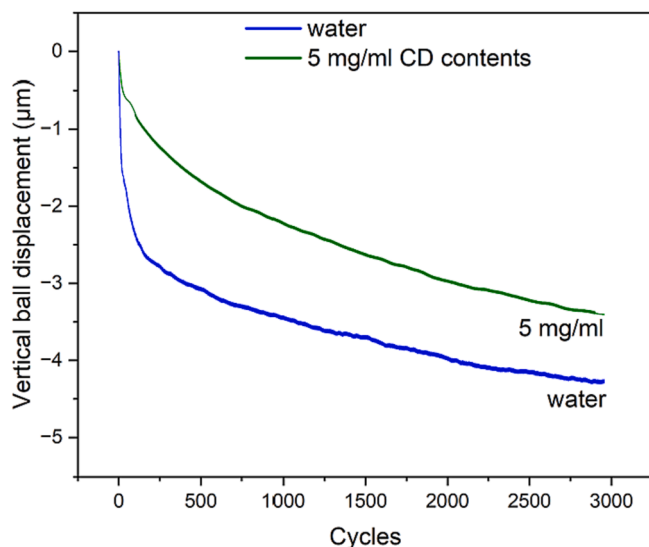


Fig. 3. Vertical ball displacement as a function of cycles at 30 N.

$\text{N}\cdot\text{m}$  to  $1.57 \times 10^{-15} \text{ m}^3/\text{N}\cdot\text{m}$ . This behavior has already been observed in a polyethylene glycol based lubricant [18]. The 3D profile (Fig. 2f) exhibits a sphere-on-plane contact geometry. Moreover, Fig. 3 shows a regular vertical displacement of the ball of up to  $3.4 \mu\text{m}$  during the experiment.

Surface lubrication with water or water with 5 mg/ml CD contents led to similar total wear volume as a function of normal load, but which was distributed in different ways (Fig. 2c and d). As a consequence, the wear rates were also similar. It has been shown by analyzing the contact geometry and the kinetic vertical displacement of the ball during the experiments that the wear mechanisms are different. Moreover, the total vertical displacement of the ball considering the wear depth of the plane, the height of the worn spherical cap, and the pull-up due to the plastic deformation of the plane, is 30 % lower with the lubricant containing 5 mg/ml CD contents than with the pure water-based one, demonstrating the good antiwear properties of CD additives.

#### 4. Conclusions

In this study, CDs were synthesized from Sargassum seaweeds. Functional groups of CD surfaces were evidenced by FTIR. Raman spectroscopy revealed that the CDs are characterized by poorly organized carbon structures. Tribological experiments revealed excellent tribological performances, as well as low COF values (0.11) and wear rates ( $1.57 \times 10^{-15} \text{ m}^3/\text{N}\cdot\text{m}$ ) associated with the use of a lubricant containing pure water with 5 mg/ml CD contents. This was due to the formation of a homogeneous carbon film on surface of the plane which helped prevent corrosion. Wear rate is commonly used to evaluate material wear but the knowledge of contact shape and vertical displacement of a ball during tribological tests is a powerful discriminant parameter for comparing different lubricant performances. The interpretation of the vertical displacement of a ball in terms of wear kinetics

still require further investigation.

#### CRediT authorship contribution statement

**P. Bilas:** Conceptualization, Methodology, Investigation, Validation, Data curation, Supervision, Writing – original draft, Writing – review & editing. **N. Nomède-Martyr:** Methodology, Investigation. **G. Mathieux:** Investigation. **Y. Bercion:** Software, Conceptualization, Methodology, Investigation. **T. Césaire:** Funding acquisition. **P. Thomas:** Writing – review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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