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Comparative study of tribological properties of vegetable oils added with pristine and fluorinated carbon nanofibers as additives in dodecane

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ABSTRACT – Conventional liquid lubricants are constituted of a base oil and (nano)additives presenting specific properties, such as friction reduction and antiwear performances. Commercial lubricants generally use mineral oils due to their well-known lubricating properties, their stability and especially competitive prices. However, vegetable oils present significant environmental benefits. In boundary lubrication, we showed in previous studies that pristine and fluorinated carbon nanofibers are promising candidates that can be used as nano-additives for lubricants. In this study, the lubricating performances of carbon nanofibers/vegetable oil/dodecane blends are evaluated. The structure of the corresponding tribofilms are investigated by Raman spectroscopy.

1. INTRODUCTION

Conventional liquid lubricants are constituted of a base oil and (nano)additives presenting specific properties, such as friction reduction and antiwear performances. Petroleum-based oils are usually used. However, such lubricants induce health and environmental hazards due to their life cycle (low biodegradability, toxicity towards environments). Many studies are now focussed on vegetable oils to be used as additives in petroleum-based ones because of their inherent qualities like renewability, bio-degradability and non-toxicity [1,2]. The role of friction reducers is to ensure the lubricating performances in boundary lubrication regime. We showed in previous studies that fluorinated nanocarbons exhibit very good tribological properties and appear as promising friction reducers [3]. Friction coefficients weaker than those of most solid lubricants (graphite) were obtained, ranging from 0.065 to 0.085. The improvement of the friction performances observed for fluorinated carbon nanofibers is associated to the lowering of CNFs surface free energy (resulting from the fluorination of the first external graphene layers) leading to a lowering of interfibres interactions. The fluorination process progresses towards the inner layers of the nanostructures when the fluorination temperature increases. Carbon nanofibers presenting fluorination rate of 0.8 (corresponding to atomic F/C

ratio) were used in this study. The corresponding intrinsic friction coefficient in air is μ compared to $\mu = 0.14 \pm 0.02$ [4] in the case of pristine carbon nanofibers.

In order to develop green lubricants, the tribological behavior of pristine or fluorinated carbon nanofibres/vegetable oil/dodecane mixtures are investigated.

2. Methodology

The carbon nanofibres materials were synthesized from high purity (>90%) carbon nanofibres (CNFs), of 2-20 microns length, supplied by MER. Direct fluorination was carried out with pure fluorine gas flow in a Monel reactor. The fluorine rate of F/C=0.8 were obtained according to the fluorination temperature $T_F = 480^\circ\text{C}$ with constant duration of 3 h and F_2 gas flux of 10 mL min^{-1} . Fluorinated carbon nanofibres are labelled CF_x . Dodecane was used as synthetic reference oil and vegetable oils were extracted from local precursors by Phytobokaz Laboratory. Mixtures of 0.5 w% of CNFs or CF_x in vegetable oil (VO)/dodecane (1:99 and 2:98 w/w) blends were prepared. In order to homogenize and avoid the aggregation of solid particles, mixtures were dispersed during 5 min in ultrasonic bath just before the friction experiment.

The tribological properties were evaluated using an alternative ball-on-plane tribometer consisting of an AISI 52100 steel ball rubbing against an AISI 52100 steel plane on which the tested material was deposited. A normal load F_N of 10 N was applied leading to a contact diameter of 140 μm (according to Hertz's theory) and a maximum contact pressure of 1 GPa. The sliding speed was 4 mm.s^{-1} . A drop of the solution was deposited on plane surface just before the friction test. Steel balls were used with initial roughness (50 μm) whereas planes were polished with abrasive discs (roughness close to 350 μm) in order to generate multidirectional scratches favouring the presence of solid particles in the sliding contact. Balls and planes were cleaned in acetone and ethanol ultrasonic baths, allowing the elimination of pollutants and remaining abrasive particles. The tangential force F_T was measured

with a computer-based data acquisition system. The friction coefficient is defined as $\mu = F_T/F_N$.

Raman spectroscopy studies of the initial compounds and of the tribofilms were performed with a HR 800 Horiba multi-channel spectrometer using a Peltier-cooled CCD detector for signal recording. The exciting line was 532 nm wavelength line (Nd YAG laser).

3. Results and Discussion

Figure 1 presents the evolution of the friction coefficient of the CNFs/2% VO/dodecane and CF_{0.8}/2% VO/dodecane mixtures as a function of cycles number, in comparison with pure CNFs and CF_x. The friction coefficient in the presence of liquid is improved for both pristine and fluorinated nanofibres. We showed in previous studies that $\mu_{dodecane+CNFs} = \mu_{dodecane+CFx} = 0.06 \pm 0.01$. Figure 1 clearly shows that the presence of vegetable oil as additive modifies the friction properties of CNFs and CF_x/dodecane mixtures. CF_{0.8}/2% VO/dodecane mixture exhibits a very low friction coefficient (close to 0.04).

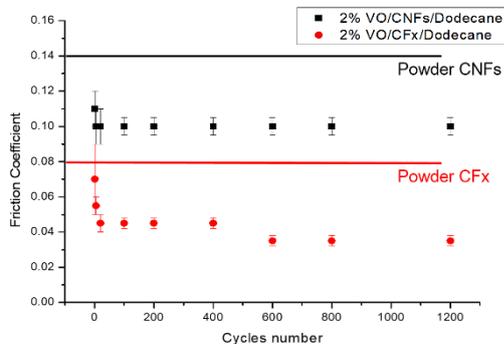


Figure 1: Evolution of friction coefficient of CNFs/2% VO/dodecane and CF_{0.8}/2% VO/dodecane mixtures as a function of cycles number, in comparison with pure CNFs and CF_x

Figure 2 shows Raman spectra recorded on CF_x powder and the tribofilm obtained for CF_{0.8}/2% VO/dodecane mixture after 1000 cycles of friction. In both cases, the vibration band at 1580 cm⁻¹ is visible, corresponding to the well-known G band associated to graphitic structure. Two bands are observed at 1345 cm⁻¹ and 1620 cm⁻¹ and are assigned to the D and D' modes. Such Raman modes appear when disorder is present in the graphitic lattice, characterizing the impurities and/or defects. Figure 2 does not evidence significant modification of the Raman spectra before and after the friction experiment, suggesting that the structure of the solid particles does not evolve during the friction process.

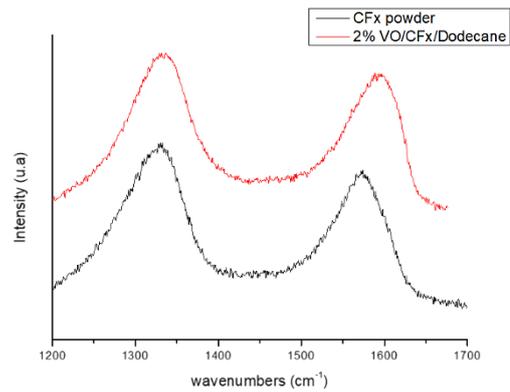


Figure 2: Raman spectra recorded on CF_x powder and on the tribofilm obtained for CF_{0.8}/2% VO/dodecane mixture after 1000 cycles of friction

4. Conclusion

This work shows that the addition of vegetable oil in fluorinated carbon nanofibres/synthetic oil blends improves the lubricating performances. Very low friction coefficients can be obtained allowing vegetable to be used as friction reduction additive in environmentally friendly liquid lubricants.

5. Acknowledgement

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6. References

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