lubricants

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Review

Ionanocarbon Lubricants. The Combination of Ionic Liquids and Carbon Nanophases in Tribology

María-Dolores Avilés, Noelia Saurín, José Sanes, Francisco-José Carrión and María-Dolores Bermúdez *

Grupo de Ciencia de Materiales e Ingeniería Metalúrgica, Departamento de Ingeniería de Materiales y Fabricación, Universidad Politécnica de Cartagena, 30202 Cartagena, Spain; mdolores.aviles@upct.es (M.-D.A.); noelia.saurin@upct.es (N.S.); pepe.sanes@upct.es (J.S.); fjc.vilches@upct.es (F.-J.C.)

* Correspondence: mdolores.bermudez@upct.es; Tel.: +34-968-325-958

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Abstract: The present overview will focus on the tribological applications of what we have called ionanocarbon lubricants, that is, the combination of carbon nanophases (graphene, carbon nanotubes, nanodiamonds, carbon nanodots) and room-temperature ionic liquids in new dispersions, blends, or modified nanostructures and their use in tribology, lubrication, and surface engineering as friction-reducing, antiwear, and surface-protecting agents in thin films and composite materials. Further research lines and factors that limit the practical applications of the outstanding research results are also highlighted. The very recent results in these lines of research make this a necessary brief review.

Keywords: carbon nanotubes; graphene; nanodiamonds; carbon nanodots; ionic liquids; friction; lubrication; wear; surfaces; interfaces

1. Room-Temperature Ionic Liquid Lubricants and Additives

Room temperature ionic liquids (ILs) have demonstrated great potential for many chemical and engineering fields, including tribology and lubrication [1–18]. Although most research efforts during the first decade of the 21st century were focused on the use of ILs as neat lubricants, our research group reported the use of ILs as lubricant additives since our first works on the subject [14–16]. The use of ILs as lubricant additives is one of the main topics of interest at the present moment [13,19–22].

Some important research lines which are being pursued at present are the substitution of the conventional aprotic halogen-derived ILs by more environmentally friendly halogen-free protic or aprotic ILs, and the combination of ILs with nanophases to create synergistic effects with enhanced friction-reducing, antiwear, and surface protective performances [18].

2. Carbon-Derived Materials in Tribology

Organic synthetic lubricants have been widely used for a long period of time, however research on their tribological performance is producing new knowledge which opens new lines of research and development. Very recently, Erdemir et al. [23] have demonstrated that, under operating conditions, lubricating oils form tribofilms similar to DLC (diamond-like carbon). The proposed mechanism consists of the catalytic dehydrogenation of the linear olefins present in the lubricating oils by nanocrystalline coating materials, followed by carbon–carbon bond cleavage and recombination to grow the amorphous anti-wear lubricating films.

These results show the relevance of carbon phases and materials in tribology, even in the absence of carbon-derived additives. The importance of carbon materials and carbon tribofilms has been further highlighted by Berman et al. [24], where an “all-carbon” system formed by the combination of graphene and nanodiamonds shows "superlubricity" of DLC, to reach an ultralow friction coefficient value of 0.004. The combined carbon nanophases form "nanoscrolls", which do not appear in the presence of water, thus inhibiting superlubricity, with the corresponding friction increase (Figure 1).

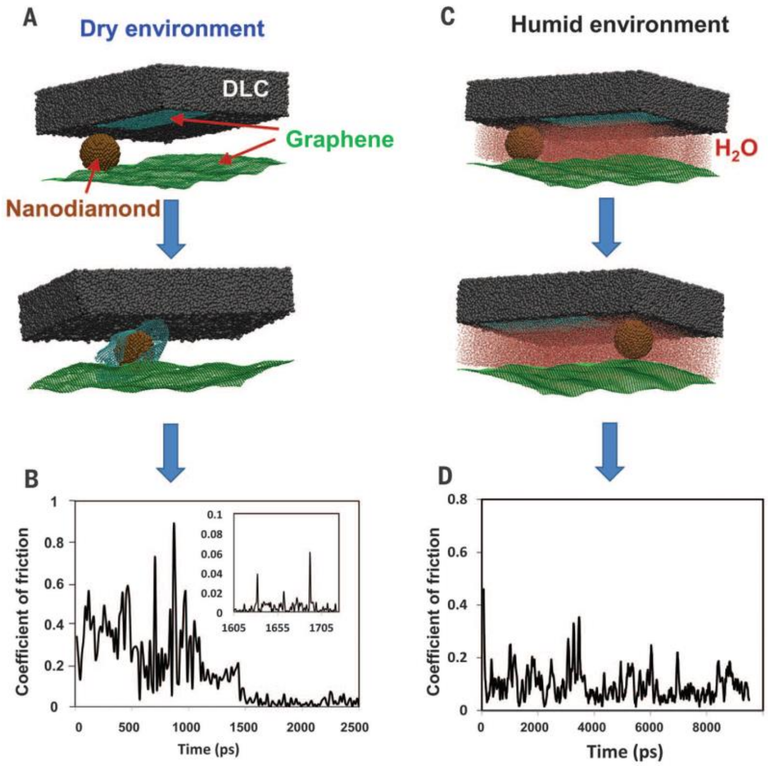


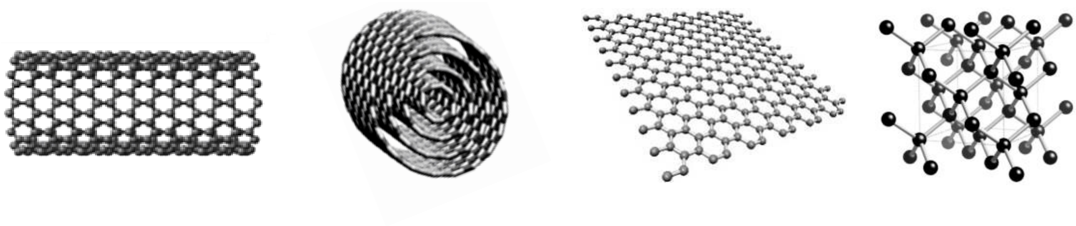
Figure 1. Reproduced from reference [24]. Reprinted with permission from AAAS.

Berman et al. [25] have also demonstrated that, in the case of graphene, quality and purity of the material is crucial for the reduction of lateral forces. In a similar way, a dramatic increase in friction was observed when graphene is oxidized. The same authors [25] have confirmed that ultralow-friction can be achieved for single layer graphene films grown by chemical vapor deposition (CVD) on silicon dioxide. This result is explained by the good adhesion of the CVD-produced graphene to the substrate, thus highlighting the influence of the manufacturing method on the tribological performance of carbon nanophases.

All above commented results show the separate relevance of ionic liquids and carbon nanophases in tribology [26–28]. In a very recent review [29], we highlighted the combination of ionic liquids and nanomaterials, from metal and ceramic nanoparticles to some carbon nanophases, with emphasis on carbon nanotubes and graphene materials. The present review will focus on the tribological applications of the new IL-carbon nanophase hybrid nanomaterials, which we have called ionanocarbon lubricants, in order to distinguish them from "ionic nanofluids", containing ILs, and from 'carbon nanofluids', containing carbon nanomaterials with fluids other than ILs.

3. Ionanocarbon Lubricants

In this section, different carbon nanomaterials will be introduced (Figure 2) and the interactions between ILs and carbon nanophases will be analyzed to interpret their tribological performance.



(**a**) (**b**) (**c**) (**d**)

Figure 2. Different forms of carbon nanophases: (**a**) Single-walled carbon nonotube; (**b**) multi-walled carbon nanotube; (**c**) graphene; (**d**) nanodiamond.

Simulation studies by molecular dynamics [30] have shown that although ILs cannot disperse bundled single-walled carbon nanotubes (SWCNTs), the interactions of IL cations with the nanotube surface can disperse up to seven aggregated non-bundled nanotubes.

Mechanical grinding of carbon nanotubes in different ILs [31] has provided a simple method to obtain new dispersions and gels [32] which has recently been extended to other carbon nanophases such as graphene or nanodiamonds [33].

Fan et al. [34] showed that carbon nanotube-IL gels can present a high conductivity and good tribological performance. This behavior was attributed to the modification of carbon nanotubes by van der Waals and π–π interactions with IL cations. A synergistic enhancement of the lubrication ability of ILs and carbon nanotubes was found.

Nanocomposites with different IL contents were obtained by interactions between IL and multi-walled carbon nanotubes (MWCNTs) [35]. Ding et al. proposed that instead of a cation-π interaction, the main interaction would be a CH–π hydrogen bond, in which the CH in the position 2 of the IL imidazolium cation acts as proton donor and the π bonds in the carbon nanotubes act as proton acceptors (see Figure 3). In the model proposed, there would be one layer of IL cations strongly interacting with the carbon nanotube, and a second layer more weakly attached (Figure 3). As new ILs are being described and used in combination with nanophases, more studies are needed in order to establish a general model of IL–carbon nanophase interaction.

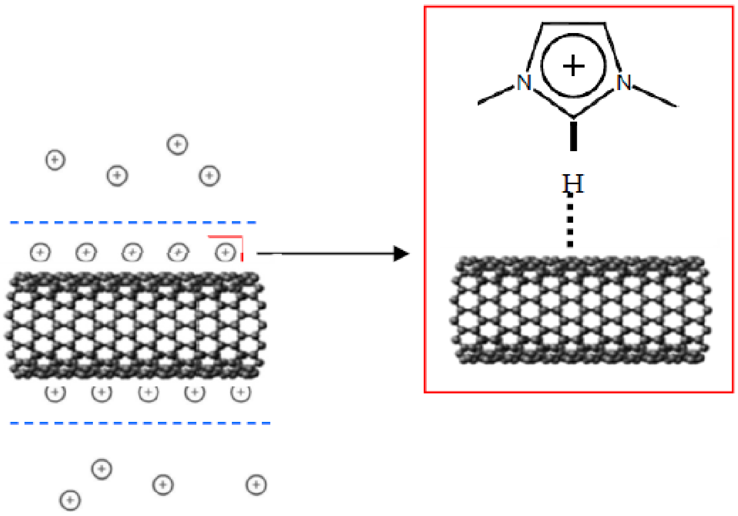


Figure 3. Illustration of the proposed interaction between imidazolium cations and carbon nanotubes [35].

W. Liu and coworkers [36] used MWCNTs, previously modified with a tetrafluoroborate imidazolium IL, as additives of another tetrafluoroborate imidazolium IL as base lubricant, reporting excellent anti-wear behavior.

The ability of ionic liquids to interact with carbon nanophases may allow even the transformation of one type of carbon nanophase into another. Kleinschmidt et al. [37] showed the opening and unrolling of carbon nanotubes to obtain graphene nanostructures, in a process that depends on the ionic liquid. Finally, these authors described the preparation of epoxy matrix nanocomposites with the new carbon nanofillers.

Dispersions of MWCNTs in ILs were also used as lubricants in polymer–steel contacts [38], showing that the addition of the carbon nanophase can lower the friction coefficients and prevent surface damage. Polymer-matrix nanocomposite materials with ionic liquid-modified carbon nanotubes have been developed [39]. In the case of the brittle polystyrene matrix, the addition of multiwalled carbon nanotubes [40] in a 1 wt % proportion reduces both friction coefficient and abrasion damage under severe scratch conditions.

The synergistic effect of the combination of SWCNT and ILs has also been applied to improve the tribological performance of brittle thermosets such as epoxy resin [41], by reducing friction and wear and increasing the thermal stability and crosslink density of the epoxy resin.

Among their varied emerging applications [42], graphene and related 2D carbon nanomaterials have been studied as additives in lubricants [43]—either oils or greases—resulting in friction and wear reduction and improving the load-carrying ability of the basestocks.

Graphene nanosheets have been used as lubricant additives [44] on steel textured surfaces, finding a synergistic effect which could be explained due to shearing of the graphene layers at the interfaces and formation of a protective film related to the texture patterns on the surface.

Fan et al. [44] obtained better results when using multilayered graphene as an additive in grease, as compared with ionic liquid or graphite. This better tribological performance was attributed to the formation of a boundary lubricating film.

Recently, different research groups have studied the combination of graphene and ionic liquids in lubrication and tribology [42–44]. It has been shown [45] that IL molecules interact with graphene nanophases, producing new dispersions with a remarkable change in the physical properties of the nanofluid with respect to pristine IL. Low concentration stable graphene dispersions in IL can reduce the viscosity by reducing the internal friction between molecules and the cation–anion interactions.

Fan et al. [46] used imidazolium ILs with fluorine-containing anions to obtain modified graphene oxide and exfoliated graphene, which were then used as lubricant additives. The excellent antiwear performance was attributed to the formation of IL-containing graphene tribofilms inside the wear tracks, which would prevent the direct contact between asperities.

Khare et al. [47] used imidazolium halogen salts, in particular, the highly viscous 1-butyl-3-methylimidazolium iodide to develop new graphene-IL nanolubricants. The tribological performance was again explained by interactions between the solid and fluid phases that changed the physicochemical and structural features of the IL.

The effect of graphene structure has been analyzed by Saurin et al. [48] by comparing two forms of commercial graphene nanomaterials—1–2 layer and 1–10 layer graphene, respectively—as additives in 1-octyl-3-methylimidazolim tetrafluoroborate in steel-epoxy resin and sapphire-steel contacts. 1–2 layered graphene gave rise to abrasive wear due to the formation of large agglomerates, while 1–10 layered graphene prevents wear by avoiding direct contact between asperities.

In situ fabrication of functionalized graphene sheets by electrochemical exfoliation of graphite in an imidazolium tetrafluoroborate ionic liquid solvent has been proposed [49] as a method to overcome the two principal problems in the development of graphene as lubricant additive, that is, their low dispersibility and the low stability of the dispersions in the long-term. Again, synergies between ILs and multilayer graphene to form physically adsorbed films and tribo-chemical reaction film are proposed as mechanisms for the enhancement of tribological performances.

IL-graphene hybrid ionic nanomaterials were developed by Gusain et al. [50] by generating covalent bonds between the imidazolium rings of the ILs and graphene. This covalent functionalization enabled the dispersion of graphene in polyethyleneglycol, used as base lubricant, thus reducing both friction coefficients and wear rates by inhibiting material loss. The authors proposed the formation of thin protective tribofilms on the sliding surfaces.

In epoxy matrix nanocomposites, Saurin et al. [51] have compared the friction and wear reductions of graphene and 1-octyl-3-methylimidazolium tetrafluorobotate IL additives separately, with those obtained for a mixture of both, with respect to unmodified epoxy resin. The higher friction and wear reduction were achieved for epoxy resin + graphene nanocomposite. This result could be explained by the opposite effects of each additive. The addition, IL produces a plasticizing effect, while graphene increases thermal stability and stiffness of the thermoset matrix, thus limiting surface damage.

The combination of different carbon nanophases with ILs has lead to a better performance than those found for each of them separately [52]. Zhang et al. [52,53] described this kind of synergistic effect between graphene oxide and multiwalled carbon nanotubes in reducing friction and wear of diamond-like carbon surfaces, even under high vacuum conditions. The proposed mechanism is the intercalation of the nanotubes between graphene layers to keep them exfoliated [29].

Even smaller carbon nanophase materials, such as carbon nanodots—defined as a new carbon nanomaterial with a size below 10 nm—have been only very recently described [54]. However, Wang et al. [55] have already reported their application in tribology in combination with ILs. Carbon nanodots capped by an IL have been synthesized and dispersed in polyethyleneglycol. Four-ball lubrication tests showed the friction reducing and antiwear ability of these new additives by a proposed combined mechanism of IL lubrication with the rolling, mending, and polishing effects of the carbon nanodots.

4. Thin Films and Coatings

Deposition of thin films and coatings are other research lines where carbon nanophases and ILs are finding applications.

The dip-coating deposition of IL-graphene composite thin film on a silicon substrate has been described [56]. The composite film improved the friction-reducing ability of the corresponding graphene-free film containing only IL. This behavior was attributed to a synergistic effect between the properties of the IL and graphene. In contrast, the hybrid IL-graphene composite film showed a lower wear resistance than the graphene-free IL film. The authors proposed that this is due to the fact that IL films become more discontinuous with the incorporation of graphene powder, as shown by SEM. This discontinuity would not prevent direct contact between the sliding materials.

Liu et al. [57], prepared DLC/IL/graphene composite coatings with different graphene concentrations, and studied their performance under high vacuum and space radiation conditions. The results showed that the addition of excess graphene to the IL would form irreversible agglomerates, finding an optimum graphene concentration of 0.075 mg mL^{-1} in IL for the best tribological performance in a simulated space environment. XPS spectra confirmed the formation of a fluorinated oil-containing carbon-rich tribofilm.

Epoxy-PTFE coatings containing graphene oxide and 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ionic liquid [58] showed synergistic effects on the tribological behavior. It was proposed that the plasticizing effect of the ionic liquid increased the contact area, generating a boundary-lubrication regime. Under these conditions graphene oxide nanoplatelets orient and reduce their abrasive behavior, contributing to a lowered coefficient of friction.

5. Conclusions

The main conclusions of the present overview may be summarized as follows:

- The best tribological performances have been attributed to synergy between the ionic liquid fluid phase and the solid nanophase tribolayers.

- Most of the research on ionanocarbon lubricants has focused on the use of halogen-containing ionic liquids and carbon nanotubes. Different graphene nanomaterials and combinations of nanotubes and graphene with ionic liquids have also shown outstanding performances.
- The studies on thin film or composite coatings are still very limited, but show a promising outlook.

6. Future Research towards Applications

The applications of carbon nanomaterials and ionic liquids to develop new ionanocarbon materials are just beginning of what is to be explored. Some key issues such as the nature of the nanophases, from their synthetic routes to the stability of their dispersions, need to be further investigated.

One of the major problems in determining the state of the advances at the present moment is the very different materials which are described with the same denomination. The so-called graphene can be anything from partially exfoliated graphite to graphene oxide or mixtures of different nanophases with amorphous carbon.

The exact nature of the interactions between the nanophases and the ionic liquids is another aspect that also needs to be studied in depth. If hybrid carbon nanophase-ionic liquid materials are to be applied in such extremely complex fields as tribology and lubrication, it is necessary to take into account the changing nature of the interactions and the stability of the dispersions under operating conditions.

The delay in the development of industrial applications of the very promising research results could be attributed to several factors, one of the most relevant is doubtless the problems of agglomeration of the nanophases [59], which can change the lubrication regime and increase wear due to abrasion.

There is an urgent need for optimization of the nanophase concentration, not only to achieve long-term stability, but also to control its influence on thermophysical and tribochemical properties of the nanofluid.

The advent of new carbon nanomaterials and their synergy with other carbon nanophases and with ionic liquids allows the prediction of a brilliant future in this research field with a predicted deep impact in tribology.

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