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Antiwear performance of ionic liquid+graphene dispersions with anomalous viscosity-temperature behavior

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ABSTRACT

New dispersions of few-layers graphene (G) in 1-ethyl-3-methylimidazolium ([EMIM]) ionic liquids (ILs) with dicyanamide ([DCA]) or bis(trifluoromethylsulfonyl)imide ([TFSI]) anions have been obtained by mechanical mixing and sonication. IL+0.5 wt% G dispersions show constant viscosity values from 357K (for IL = [EMIM][DCA]) or from 385K (for IL = [EMIM][TFSI]) to 393K. IL + G dispersions with G > 0.5 wt% show linear viscosity increases with increasing temperature, from 306K (for [EMIM][DCA]+1 wt%G) and from 330K to 393K (for [EMIM][TFSI]+0.75 wt%G and [EMIM][TFSI]+1 wt%G). Addition of graphene improves the poor wear reducing performance of [EMIM][DCA], and prevents surface damage on steel when added to [EMIM][TFSI]. Graphene increases the load-carrying ability of ILs, forms a surface layer on the sliding path and retains wear debris, preventing the formation of large abrasive particles.

1. Introduction

Room-temperature ionic liquids (ILs) are molten salts with melting points below room temperature, which are generally formed by a combination of organic cations and organic or inorganic weakly coordinating anions. These ordered fluids present properties such as negligible vapor pressure, large liquid range, high thermal stability and ionic conductivity, which have attracted a growing interest in many scientific and technical fields, including lubrication and surface engineering [1–8]. The origin of ionic liquids can be traced back to XIX century, although the first protic ionic liquid, ethylammonium nitrate, was reported by Walden in 1914 [9]. However, it was not until 1992 that Wilkes and Zawarotko reported the first room-temperature ionic liquids which were stable in air and in water, the alkylimidazolium derivatives with the tetrafluoroborate or hexafluorophosphate anions [10]. The first report on the low friction coefficients afforded by fluorine-containing imidazolium ILs on a variety of contacts dates from 2001 [11]. Three years later, in 2004, graphene was obtained [12]. Graphene, a flat monolayer of sp^2 carbon atoms, is presently one of the most widely investigated materials due to its unique structure, properties and potential applications [13]. The applications of graphene for tribological purposes have been a very active field of research in recent years [14,15].

It has been reported that non-polar lubricant oils cannot properly disperse graphene and, therefore, the nanomaterial must be modified [16]. Ionic liquids are excellent graphene dispersant media through van der Waals interactions and hindrance of self-assembly of the graphene plates [17]. The dispersion of graphene in ILs has been shown to achieve enhanced tribological performance [6,15,18–21]. The rheological study of ionic liquids, nanofluids and dispersions is an important aspect for their practical applications, particularly as thermal fluids and lubricants or lubricant additives [22].

For more than a decade since the first report by Ye et al. most ionic liquids studied as lubricant or lubricant additives [8,23] were composed of anions containing heteroatoms such as halogens, in particular fluorine [24] phosphorus of sulfur, which are reactive and potentially corrosive, contaminant or hazardous. In the present search for more environmentally friendly or even biocompatible formulations, a growing number of studies consider the use of, not only halogen-free, but fully organic ionic liquids [25–27]. Such is the case of alkylimidazolium dicyanamide ILs.

1-alkyl-3-methylimidazolium dicyanamide room-temperature ionic liquids were first reported by MacFarlane et al. [27], and have been used as dispersants for single-walled carbon nanotubes (SWCNTs) [28,29] and as initiators of epoxy polymerization in nanocomposites [30].

Imidazolium ILs with the dicyanamide anion exhibit lower density and viscosity than ILs containing other anions [31]. In particular, [EMIM][DCA] is the ionic liquid with the lowest viscosity at 298 K [32], presents

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Newtonian behavior over the range of shear rates from 10 to 10^3 s^{-1}, and a viscosity decrease with temperature [33], as expected.

Low concentrations (0.03%) of graphene or graphene oxide reduce the viscosity of 1-butyl-3-methylimidazolium dicyanamide ([BMIM][DCA]) in the temperature range between 0 and 20 °C. In all cases, viscosity decreased with increasing temperature [34].

The rheological behavior and tribological applications of graphene-based nanofluids are currently the subject of much interest [35] and have been recently reviewed [36]. Several recent studies have addressed the problem of graphene-IL interactions, in particular for [EMIM]-derived ILs [37,38].

1-ethyl-3-methylimidazolium dicyanamide has been described as inhibitor of steel corrosion [39], where the dicyanamide anion controls surface film formation. This precedent could anticipate also a good lubricating performance for steel. Previous reports on the tribological performance of [DCA]-derived ILs are very scarce [40,41].

A simple relationship between fluidity, defined as the inverse of viscosity, and temperature has been described [42]. Fluidity and ionic conductivity decrease as alkyl chain lengths increase. This has been attributed to the increase in the van der Waals interactions between alkyl chains [43].

The highly non-spherical [DCA] anion [44] would generate a lower intermolecular friction than spherical anions such as [BF_4]. Thus, the combination of the short alkyl chain [EMIM] cation and the non-spherical DCA anion gives rise to low viscosity, high fluidity ionic liquid [45].

The rheological behavior and tribological performance of the halogen-free [EMIM][DCA] and its graphene dispersions has been compared with that of [EMIM][TFSI], with the fluorinated, sulfur-containing bis(trifluoromehylsulfonyl)imide anion, which has been the object of interest in lubrication studies [46].

2. Experimental

Ionic liquids 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([EMIM][TFSI]) (Fig. 1) (purity > 98%) and graphene (1–10 layers; purity > 99%) (Fig. 2) were commercially available from Iolitec (Ionic Liquids Technologies GmbH, Germany).

The procedure for the preparation of the dispersions of graphene in ILs consisted in the addition of graphene to the ionic liquid in 0.5 or 1.0 wt% proportions following the method described in previous works [20,21,47,48], by mechanical milling in an agate mortar for 10 min, followed by sonication for 30 min.

The stability of the dispersions was monitorized before and after each rheological test in order to ensure the absence of phase segregation. The dispersions were stable at room temperature for a period of at least 2 months (Fig. S1, Supporting Information).

The rheological behavior of pure ionic liquids and the dispersion was determined using an AR-G2 rotational rheometer from TA instruments (New Castle, Delawere, USA) [28]. The instrument was calibrated (Fig. S2, Supporting Information) previously to the realization of rheological tests.

All experiments were carried out at least three times with a plate-plate configuration and the temperature was controlled by a Peltier system with an accuracy of ±0.1 °C, using a plate-plate configuration with a diameter of the rotational plate of 60 mm and a gap between plates of 1000 μm.

The shear flow influence on the viscosity was studied at 25 °C by increasing the shear rate from 10^{-3} to 500 s^{-1} in steady state.

The temperature dependence was evaluated with a reversible temperature ramp from 298 to 398 °C at a constant shear rate of 50 s^{-1}. The heating and cooling speed was set to 1 °C/min.

Tribological tests were carried out in a pin-on-disk tribometer (Anton Parr; Masó Analitica, Spain) under ambient conditions (25±1 °C; HR: 50–60%). The materials used in tribological tests [49] were sapphire balls (Al_2O_3 99.9%; hardness: 2750 HV) with 0.75 mm sphere radius and AISI 316L stainless steel (nominal composition in weight percentage: <0.03 C; 16–18.5 Cr; 10–14 Ni; 2–3 Mo; <2 Mn; <1 Si; <0.045 P; <0.03 S; balance Fe); hardness: 195 HV) discs (25 mm diameter; 2.5 mm thickness). Before the tests, steel discs were polished to a final average surface roughness (Ra) of 0.12–0.13 μm, determined by means of a SM7 Profiltest contact profiler. A 0.5 mL lubricant volume was used, under a load of 0.98 N (mean contact pressure 1.30 GPa; maximum contact pressure 1.95 GPa), at a speed of 0.1 m/s (sliding radius 9 mm), and a total sliding distance of 1500 m.

Wear tracks sections and volumes were determined with a Talysurf CLI 3D optical profiler.

Optical micrographs were obtained using a Leica DMRX optical microscope. SEM micrographs and EDX element maps were obtained with a Hitachi S-3500N.

Raman spectroscopy and transmission electron microscopy (TEM) techniques have been previously described [28].

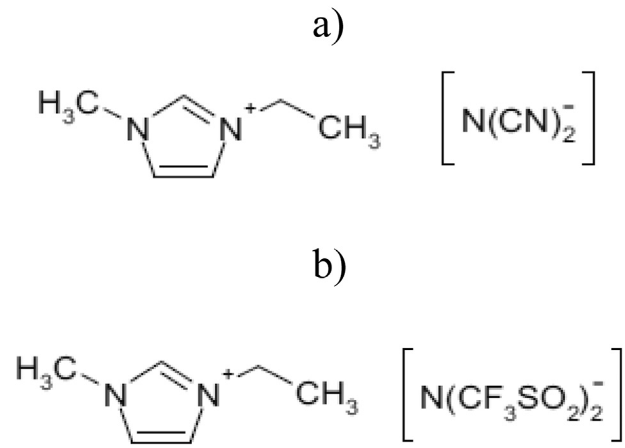

Fig. 1. Ionic liquids: a) 1-ethyl-3-methylimidazolium dicyanamide; b) 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide.

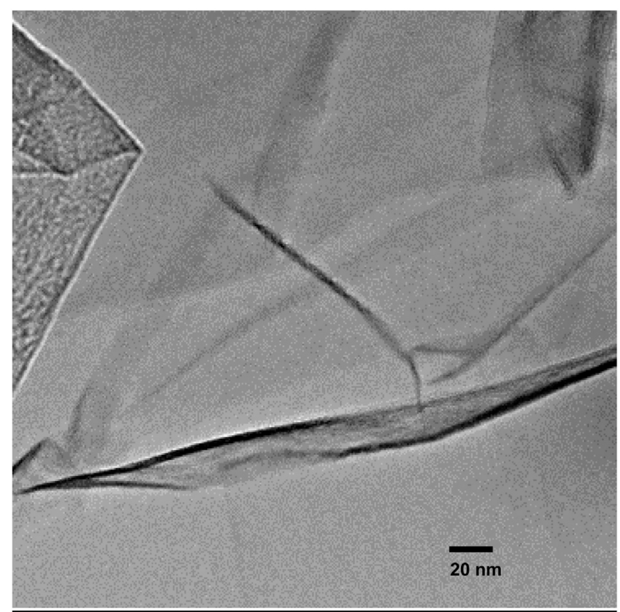

Fig. 2. TEM micrograph of as-received graphene.