

Rheological study of new dispersions of Carbon Nanotubes in the ionic liquid 1-ethyl-3-methylimidazolium dicyanamide

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ABSTRACT

Dispersions of three different types of carbon nanotubes in a 1 wt.% proportion in the low viscosity 1-ethyl-3-methylimidazolium ([EMIM][DCA]) ionic liquid have been obtained. The neat ionic liquid presents Newtonian behavior, but the addition of carbon nanotubes increases the viscosity with respect to [EMIM][DCA] in the following order: Single-Walled Carbon Nanotubes (SWCNTs) > aligned Multi-Walled Carbon Nanotubes (aligned-MWCNTs) > Multi-Walled Carbon Nanotubes (MWCNTs), and the resulting fluids show non-Newtonian behavior. SWCNTs and MWCNTs dispersions present shear thinning with increasing shear rate, but a shear thickening effect for aligned-MWCNTs at intermediate shear rate values at room temperature has been observed. This effect disappears at 100 °C. The thermal response of the viscosity of [EMIM][DCA] and the CNTs-IL dispersions can be fitted to the Arrhenius model. For [EMIM][DCA] and the dispersion with MWCNTs the viscous behavior prevails at low frequencies, with a cross point at a critical frequency value which decreases with increasing temperature. However, the dispersions of SWCNTs and aligned-MWCNTs present storage modulus values higher than loss modulus in the whole range of frequency.

Keywords: Carbon Nanotubes; ionic liquid; rheology; viscoelasticity; Raman; non-Newtonian fluids.

INTRODUCTION

In the recent years, carbon nanophases such as graphene, carbon nanotubes, carbon nanofibers, carbon nanohorns, nanodiamonds, nanoribbons, fullerenes, etc. have been the focus of the scientific community due to their unusual combination of mechanical, thermal and electrical properties [1]. Carbon nanotubes (CNTs), also known as buckytubes, have become an important scientific field for the extensive research due to their interesting physical properties and technological applications, such as nanoelectronics [2], energy storage [3] or sensors [4]. Single-Walled Carbon Nanotubes (SWCNTs) can be considered as a rolled-up sheet of graphene, but when the nanophase is composed of multiple concentric cylinders, it is the so-called Multi-Walled Carbon Nanotubes (MWCNTs). These structures are disorderly arranged, however there is a special aligned form with a higher degree of organization [5]. Among available nanomaterials, carbon nanotubes showed promising tribological behavior, due to the weak van de Waals forces between the sliding surfaces [6]. Particularly, Multi-Walled Carbon Nanotubes (MWCNTs) have been widely used in solid lubrication [7-9] and as lubricant additives [10,11]. However, these nanomaterials have shown a tendency to agglomerate, and their applications have been limited by their difficulty in processing. In order to achieve the best performance of these materials, it is of fundamental importance the development of new methodologies to improve their dispersion. In this sense, ionic liquids have emerged as an alternative to obtain well-dispersed carbon nanomaterials [12-14].

Ionic liquids (ILs) are molten salts at room temperature. Their recently widespread applications in different technological fields are due to their unique characteristics such as low volatility, high thermal stability, high ionic conductivity and good solvation properties, among others [15,16]. One of their main advantages is that some properties can also be adjusted to particular requirements, such as solvents for organic reactions, tailored lubricants, high-performance liquid electrolytes or composite materials derived from polymers and nanomaterials [17,18]. ILs have attracted a growing interest in the fields of materials science and engineering, tribology and lubrication technologies [19-23]. The development of large numbers of new ILs with many different technological applications and their ability to disperse the different carbon structures and nanoparticles are among their main advantages [12,24-27]. Fukushima et al. have firstly reported the preparation of CNT-IL gels, in a large scale by mechanical grinding, with applications in several fields such as sensors, actuators and electrochemistry [24,28,29]. Interest in such combinations was aroused due to the significant changes in the CNT rheological properties, the high thermal stability of the combination, and the ability to produce high conductive polymeric gel from polymerizable IL and CNT. Since then, numerous studies were performed to investigate the potential application of different types of carbon nanomaterials-IL hybrids. ILs disperse CNTs through cation- π and π - π [30,31] and van der Waals interactions without an obvious influence of the electronic structure of CNTs [32]. Moreover, it has been proved via X-ray diffraction and molecular dynamics simulations that ILs are not only present on the external nanotube surface but can be encapsulated inside CNTs [33, 34].

We have previously reported [35] the rheology and the viscoelastic behavior of aligned and non-aligned MWCNTs dispersed in [EMIM][TsO], where [EMIM] is the 1-ethyl-3-methylimidazolium cation and [TsO] is the sulfur-containing tosylate anion. Many

conventional alkyimidazolium ILs with anions containing fluorine, and/or phosphorus and sulfur have been studied as potential lubricants or lubricant additives by themselves or in combination with nanoparticles and carbon nanophases. However, the presence of such heteroatoms limits the real applications of ILs due to their hazardous potential, as they can give rise to toxic, corrosive or contaminant products [36]. In the search for an IL free from heteroatoms and with a low viscosity combined with high thermal stability, we have selected 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]), the alkyimidazolium IL with the lowest viscosity values. The present study reports the rheological behavior of dispersions of SWCNTs, non-aligned MWCNTs and aligned MWCNTs in the low viscosity [EMIM][DCA], with a halogen, phosphorus and sulfur-free anion. The [EMIM][DCA]-CNTs mixtures have been previously studied by computational simulation [37], but to the best of our knowledge, this is the first experimental evaluation of the structural properties of this kind of dispersions.

MATERIALS AND METHODS

The ionic liquid 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]) was purchased from Iolitec (Ionic Liquids Technologies GmbH, Germany) with a purity higher than 98 %. The chemical structure of the ionic liquid is shown in Figure 1. Carbon nanotubes were purchased from Nanostructured and Amorphous Materials, Inc. (Texas, USA). MWCNTs (reference number 1225YJS) have an average external diameter of 8 nm and an average length of 0.5-2 μm , with a purity of 95 %. Aligned MWCNTs (reference number 1215NMGA) present an average external diameter of 10-20 nm, with an average length of 5-15 μm , and a purity of 95 %. SWCNTs (reference number 1284YJ), have an average external diameter of 1-2 nm, 5-30 μm average length and a purity of 90 %. Figures 2a-c show transmission electron microscopy (TEM)

micrographs of the as-received carbon nanotubes where the different structures can be seen. Aligned-MWCNTs are the species with the most ordered structure of the whole CNTs series. These TEM images were obtained with a high resolution JEOL JEM 2100 microscope.

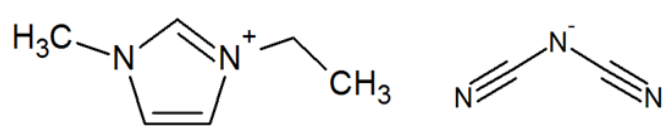


Figure 1. Chemical structure of 1-ethyl-3-methylimidazolium dicyanamide.

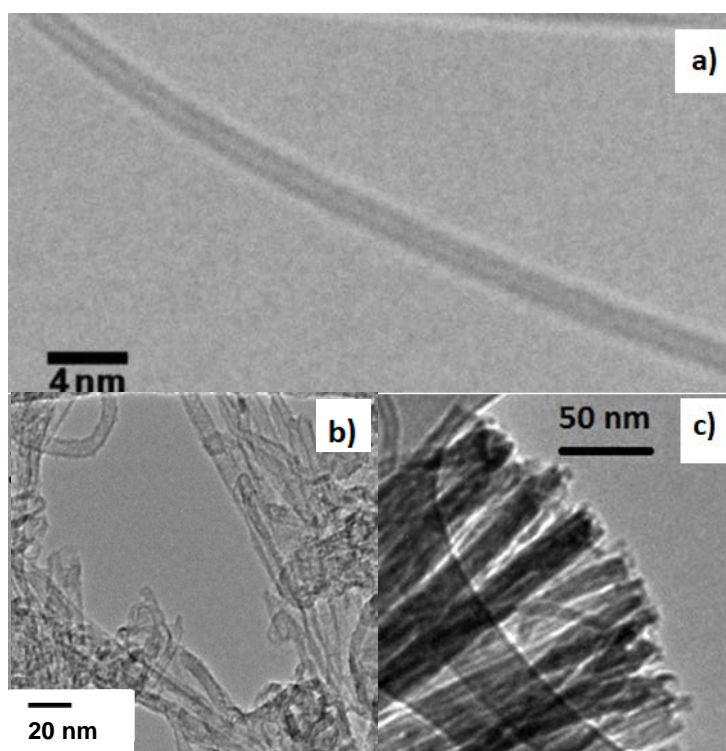


Figure 2. TEM micrographs of carbon nanophases: a) SWCNT; b) non-aligned-MWCNTs; c) aligned-MWCNTs.

Dispersions of CNTs are prepared by simple addition to the ionic liquid in a 1 wt.% proportion following the method described previously by Fukushima [28] and also used in our earlier works [26,34,38,39]. With this procedure, the materials are weighed and mixed in an agate mortar, where manual blend was performed for 10 minutes. Afterwards, the mixtures were ultrasonicated during 30 minutes at 30 °C to better disperse the carbon nanophases.

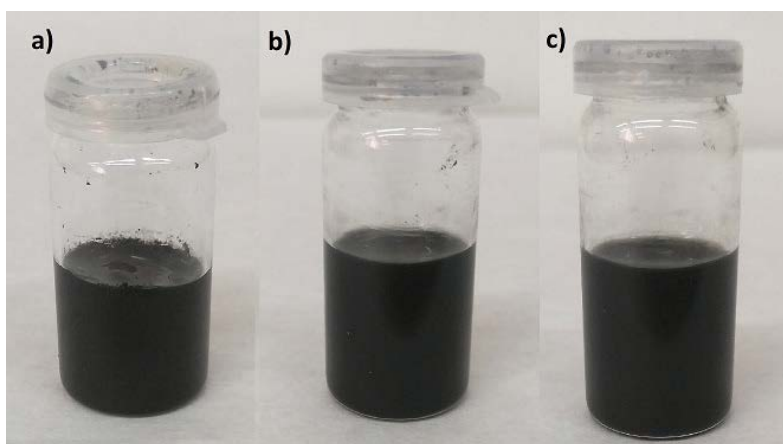


Figure 3. Dispersions of SWCNTs (a), MWCNTs (b) and aligned-MWCTNs (c) in [EMIM][DCA].

Raman spectra at room temperature were collected using a Nicolet Almega XR Raman spectrometer from Thermo Electron, equipped with an Olympus microscope. A laser of 514 nm at 100 % of power and 50 μ m of aperture was used. The rheological behavior of the [EMIM][DCA]+CNTs dispersions was evaluated using an AR-G2 rotational rheometer from TA instruments (New Castle, Delaware, USA). All experiments were carried out with a plate-plate configuration with a diameter of the rotational plate of 40 mm and a gap between plates of 1000 micrometers. The temperature control was carried out with a Peltier system which accuracy is 0.1 °C. Three different series of experiments were performed: steady-state shear flow curves, temperature ramps at a constant shear

flow and oscillation. The shear flow influence on the steady-state viscosity was studied at 25, and 100 °C by increasing the shear rate from 10^{-2} to 500 s^{-1} . To study the thermal effect on the viscosity, temperature ramps from 25 to 100 °C with a speed of 1 °C/min were carried out at a constant shear rate of 50 s^{-1} . Finally, oscillation experiments were performed employing an angular frequency range from 0.5 to 500 rad/s to evaluate the behavior of the loss and storage moduli.

RESULTS AND DISCUSSION

Raman spectroscopy

Figure 4 shows Raman spectra for [EMIM][DCA] (Figure 4a) and for as-received carbon nanotubes and the corresponding dispersions in the IL, [EMIM][DCA]+SWCNT (Figure 4b); [EMIM][DCA]+MWCNTs (Figure 4c) and [EMIM][DCA]+aligned MWCNTs (Figure 4d). For a better discussion, the main Raman bands and intensity ratios for carbon nanotubes and their dispersions in IL are collected in table 1.

In our case, the main absorptions in the Raman spectrum of neat [EMIM][DCA] (Figure 4a) are observed at 2198.4 cm^{-1} , assignable to C-N stretching of the dicyanamide anion [40] and 2949.2 cm^{-1} , assignable to C-H stretching of the imidazolium cation [41]. The first absorption is shifted to lower values, at 2192.7 cm^{-1} for the dispersions containing SWCNTs and MWCNTs, but when aligned-MWCNTs are dispersed this peak is found at 2189.9 cm^{-1} . These observations are in agreement with a stronger interaction of the IL with aligned-MWCNTs.

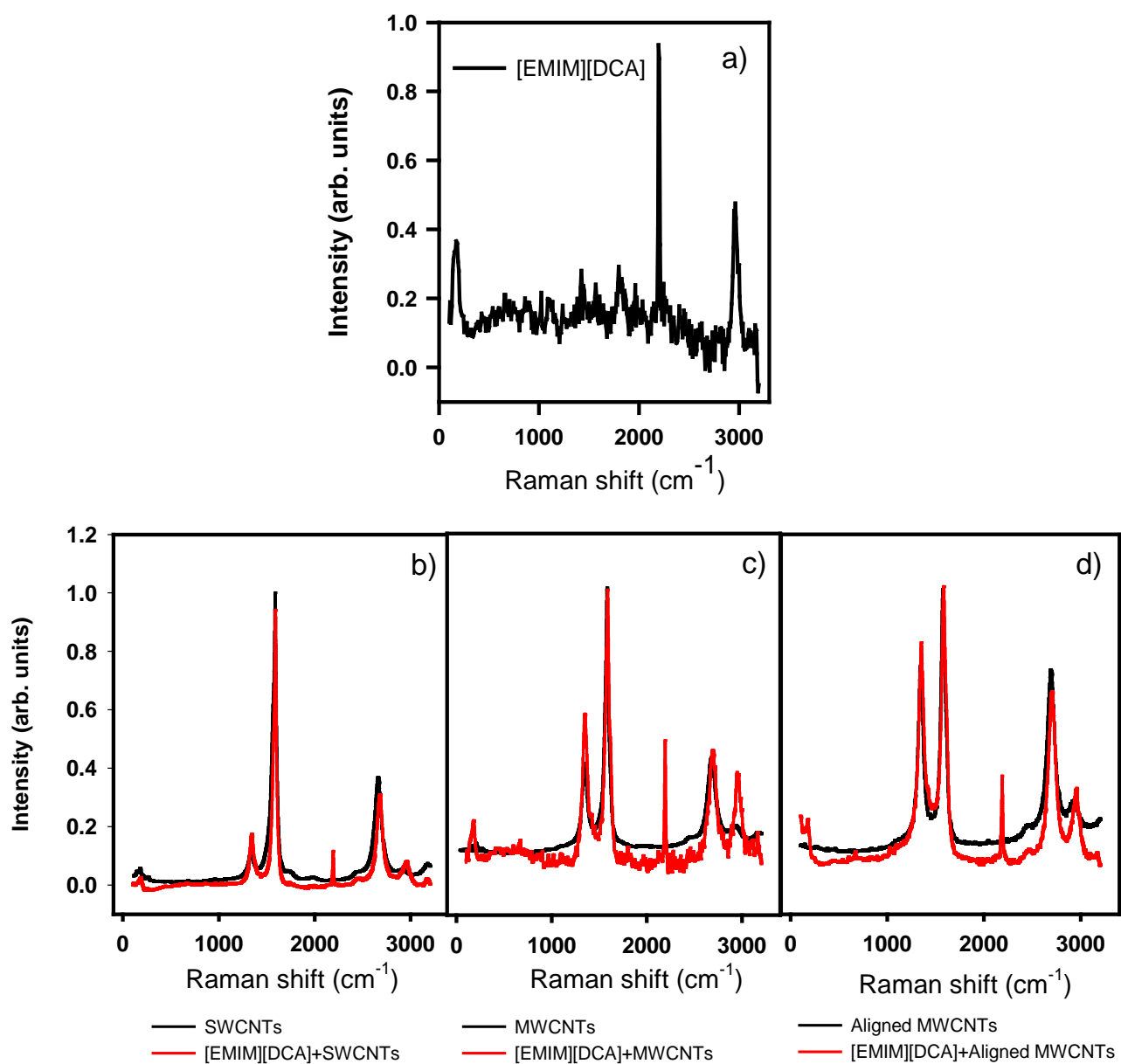


Figure 4. Raman spectra of: [EMIM][DCA] (a); SWCNTs and SWCNTs (b); MWCNTs and aligned MWCNTs (d) and their dispersions in [EMIM][DCA].

Table 1. Raman shifts (cm^{-1}) and intensity ratios for carbon nanotubes and their dispersions in [EMIM][DCA].

Raman	SWCNTs	IL+SWCNTs	MWCNTs	IL+MWCNTs	Aligned MWCNTs	IL+aligned MWCNTs
D band	1333.3	1342.8	1349.0	1347.4	1347.4	1352.0
G band	1587.6	1590.8	1580.3	1586.3	1575.8	1586.3
G'band	2660.4	2681.5	2676.2	2697.1	2694.5	2707.5
ID/IG	0.37	0.32	0.38	0.41	0.71	0.63
IG'/IG	0.12	0.18	0.36	0.51	0.73	0.80

Regarding the CNTs spectra, the D band gives information about the disorder and defects of carbon nanophases, the G band is associated to the in-plane C-C vibrations, and the G' band is an overtone of the D band. Therefore, the ID/IG and IG'/IG intensity ratios can be used to evaluate the structural order and defect density [42]. In all cases, the G band is shifted to higher wavenumber values, indicating a reduction in the interactions between nanotubes due to the presence of the ionic liquid. All nanophases show an increase in the IG'/IG ratio when they are dispersed in the ionic liquid probably due to a reduction of nanotubes ordering. On the other hand, the reduction in the ID/IG ratio observed for SWCNTs and aligned-MWCNTs could be due to a reduction of structural defects due to the interactions with IL molecules. However these increments cannot be considered statistically significant, these findings indicate a good dispersion of the CNTs in [EMIM][DCA].

Rheology. Effect of shear rate.

The shear rate effect on the steady-state viscosity of the ionic liquid [EMIM][DCA] has been studied at different temperatures. This fluid showed Newtonian behavior with a constant viscosity [43,44]. These values are 13.4 and 4.3 cP, at 25 °C and 100 °C respectively and are represented in Figure 5 as the dashed lines. The lower values

compared to the references can be ascribed to the saturation of water of this commercial ionic liquid. As expected, the addition of CNTs to [EMIM][DCA] provokes an increase in the viscosity, but also, the dispersion of carbon nanophases in [EMIM][DCA] leads to a kind of fluids with interesting Non-Newtonian behavior. Carbon nanophases present a high affinity for imidazolium cations and the formation of a better organized structure occurs. Then, the resistance to flow of these fluids is higher and the viscosity is increased. When the shear flow is raised, these structures are disrupted and the subsequent shear thinning effect is observed.

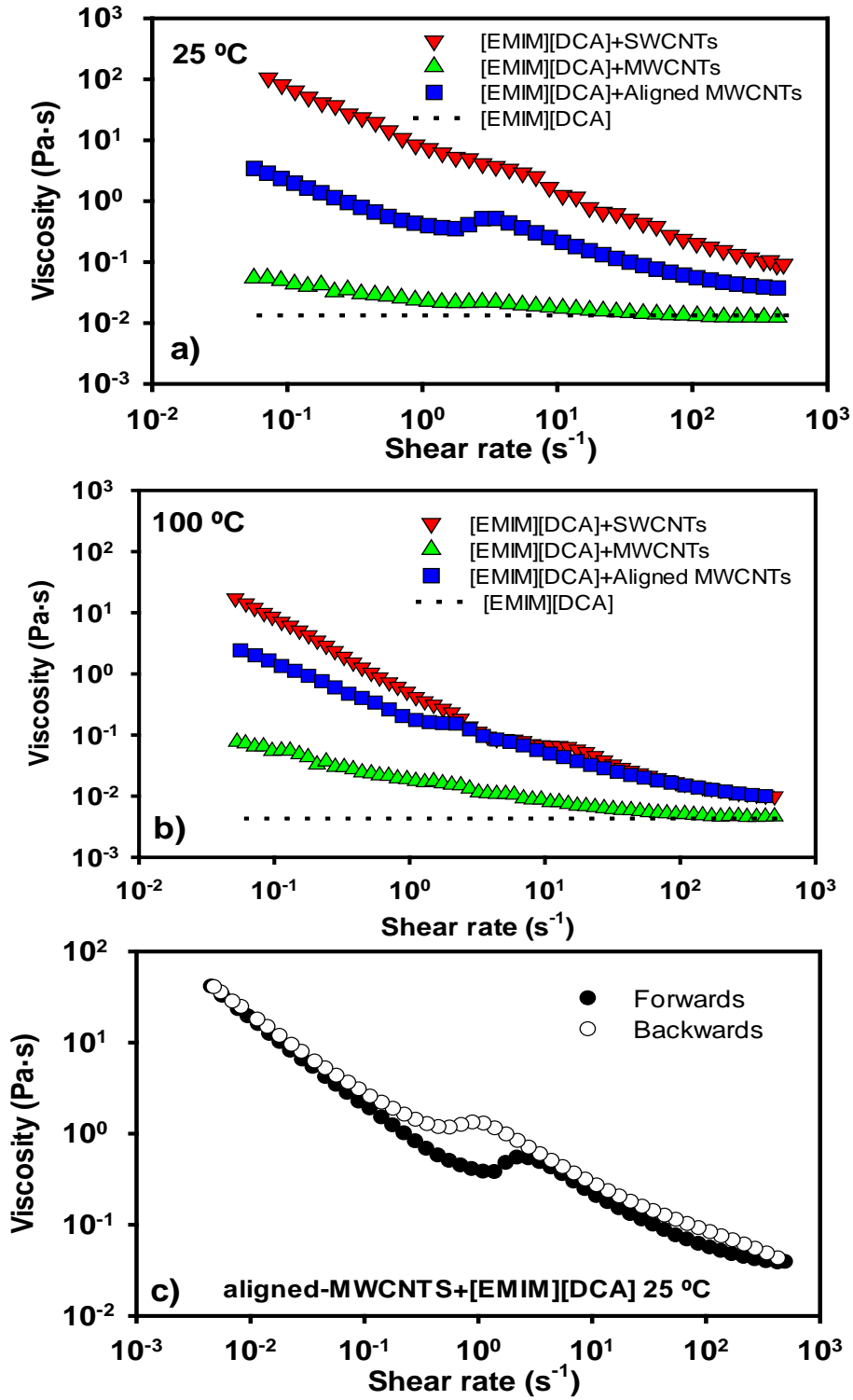


Figure 5. Viscosity values as a function of shear rate: a) at 25°C; b) at 100°C.

As it can be seen, SWCNTs cause the highest impact on the viscosity of [EMIM][DCA]. We can ascribe this elevated resistance to flow to the presence of big carbon agglomerates in the ionic liquid, since these species do have a high tendency to stick together. Interestingly, in the case of the aligned carbon nanotubes, an increase of the viscosity can be seen at intermediate flow intensities. Analogously to some polymers with tendency to agglomerate when they are dispersed in solvents, the flow facilitates the encountering of the particles dispersed in the ionic liquid and shear-induced association aggregates are formed [45,46]. These aggregates facilitate a higher resistance to flow and a shear thickening is observed. When the shear rate arrives at a value of 1 s^{-1} , the flow is high enough to interrupt the formation of aggregates and the shear thinning appears. As it can be seen in the supplemental information (Figure 5c), this effect is completely reversible. Interestingly, the shear thickening effect is not seen if the temperature is raised to $100 \text{ }^\circ\text{C}$. The interaction between the CNTs and the ionic liquid is weaker at this higher temperature and not only a viscosity diminution is seen but the formation of aggregates is interrupted by the effect of shear. On the other hand, the dispersion of MWCNTs shows a shear thinning with a Newtonian plateau at high shear values when all the intermolecular interactions are disrupted. In the case of SWCNTs and aligned-MWCNTs, this Newtonian behavior cannot be seen up to 500 s^{-1} . Indeed, in these later cases the viscosity values are superposed. Our hypothesis is that SWCNTs are aggregated and aligned by the action of flow with a similar disposal as the aligned-MWCNTs are dispersed.

Rheology. Effect of temperature.

The effect of temperature in our dispersions is depicted in Figure 6. In this experiment, a constant shear rate (50 s^{-1}) has been applied and the temperature has been increased with a velocity of $1 \text{ }^\circ\text{C}/\text{min}$. In every case, the increase of temperature causes a decrease

on the viscosity values as it was expected [47]. The data have been fitted to the Arrhenius equation [48]:

$$\eta=A\cdot[\exp(Ea/RT)], \quad (\text{eq. 1})$$

where A is the pre-exponential factor related to the viscosity at a theoretically infinite temperature, and Ea is the activation energy of the flow and R is the ideal gases universal constant. Aligned-MWCNTs, MWCNTs dispersions and [EMIM][DCA] showed a satisfactory fitting, but the quality of the data for the SWCNTs dispersion is not as good as in the other cases, as it can be seen in Table 2. This finding can be ascribed to the presence of agglomerates in this sample. In agreement with data in Figure 3, the viscosity increases with the addition of CNTs, and a larger increment is seen when SWCNTs and aligned-MWCNTs are added to [EMIM][DCA]. However, the activation energy decreases in the opposite way, with the largest value for the neat ionic liquid and the lowest value for the most viscous system. This parameter measures the temperature-dependence of the viscosity of the fluids. Then, the addition of carbon nanophases to [EMIM][DCA] reduces the effect of the temperature on the viscosity values. A higher viscosity and a better thermal stability of the values are found when CNTs are added in the following order: SWCNTs > aligned-MWCNTs > MWCNTs. Since these dispersions have potential applications as lubricants, our results anticipate an enhancement on their tribological performance.

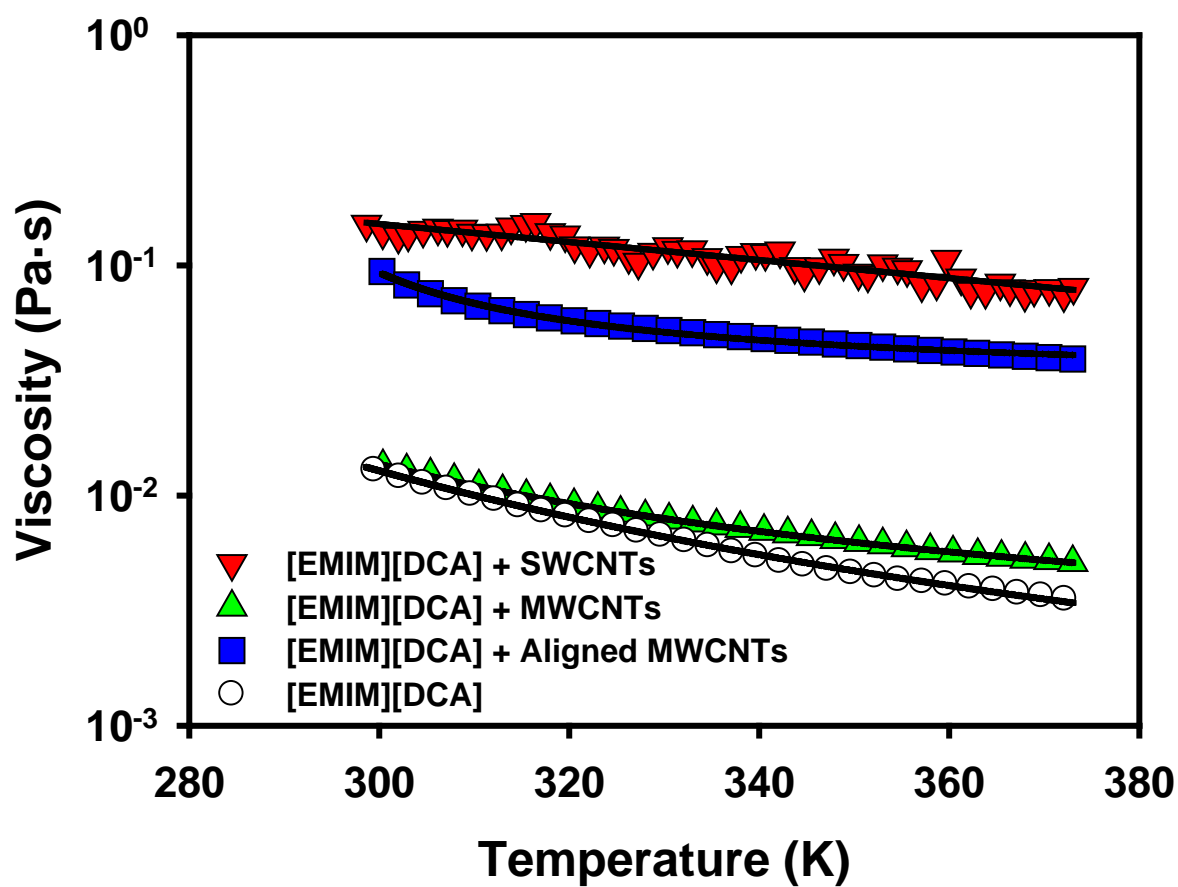


Figure 6. Variation of viscosity of [EMIM][DCA] and [EMIM][DCA]-CNTs dispersions with temperature at constant shear rate.

Table 2. Arrhenius parameters for [EMIM][DCA] and CNTs dispersions.

Dispersion	A ($\times 10^5$) (Pa·s)	Ea (kJ/mol)	r ²
[EMIM][DCA]	1.54 \pm 0.02	16.7 \pm 0.5	0.9954
[EMIM][DCA]+ MWCNTs	9.4 \pm 0.9	12.3 \pm 0.2	0.9906
[EMIM][DCA]+ aligned-MWCNTs	183 \pm 9	9.3 \pm 0.3	0.9400
[EMIM][DCA]+ SWCNTs	500 \pm 100	9 \pm 2	0.8775

Rheology. Viscoelastic behavior

We have explored the viscoelastic behavior of the IL and the dispersions at 25 °C (Figure 7a) and 100 °C (Figure 7b). Previously, the viscoelastic linear regions of the samples were determined at a constant angular frequency of 6.28 rad/s. The value of the strain at 25 °C was set to 1 % and 0.1 % in the case of 100 °C. As it can be observed in Table 3, neat [EMIM][DCA] shows frequency values where the storage modulus G' meets the loss modulus G'' . This effect is favored with increasing temperature since the crossover occurs at a lower frequency at 100 °C than at 25 °C as it is depicted in Table 3. The Cox-Merz empirical rule was tested and the superposition between the steady-state viscosity and the complex viscosity was satisfactory until the crossover values (see supplementary information, Figure S). It seems that under an elevated oscillatory stress the ionic liquid is able to form a solid-like structure at high frequencies and a deviation from the Newtonian behavior appreciated under the steady-state conditions occurs. This unexpected effect shows the ability of ILs to form highly ordered structures even in the case of low viscosity values.

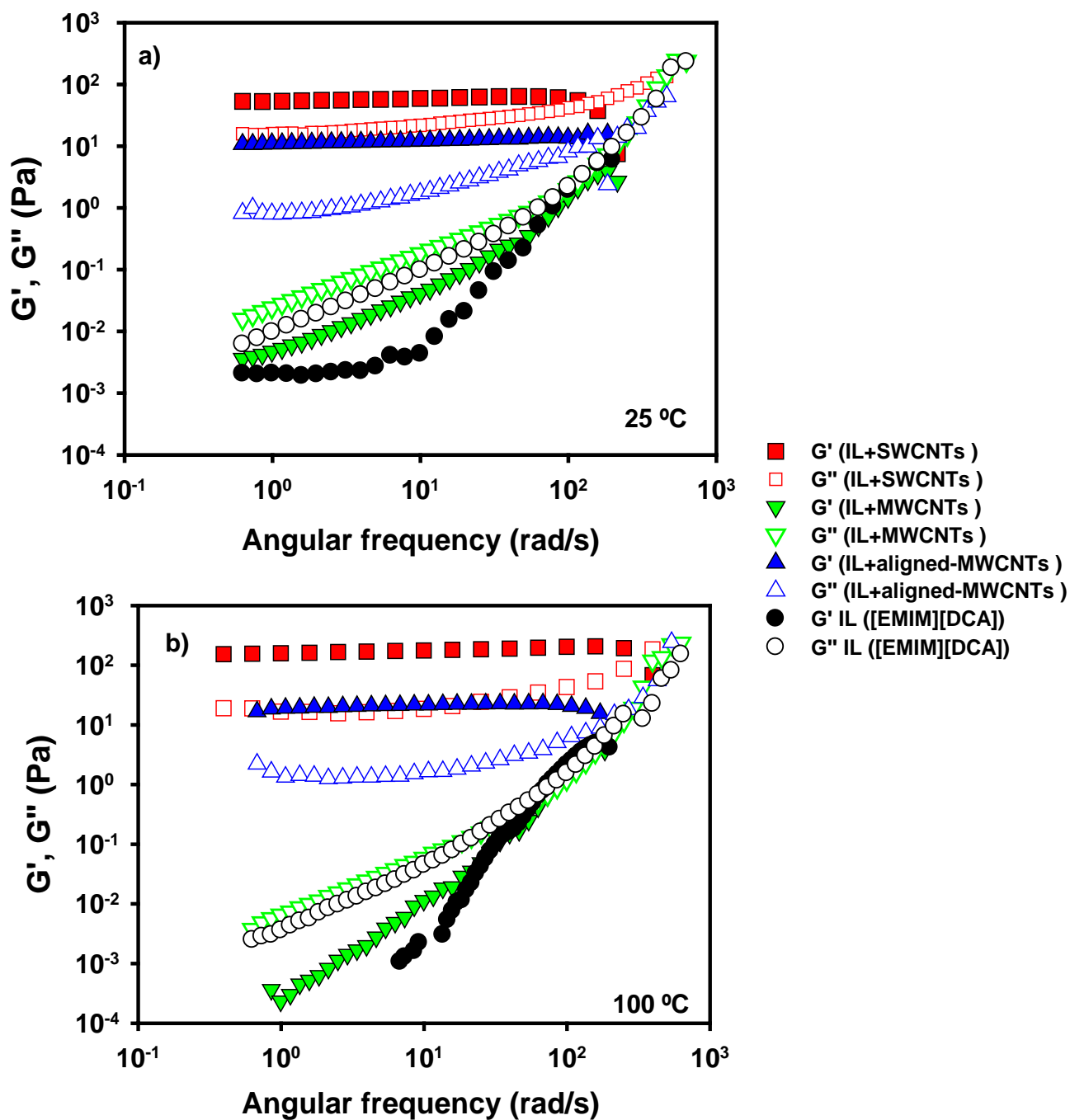


Figure 7. Variation of storage and loss moduli with frequency: a) 25 °C; b) 100 °C.

In the case of MWCNTs, at 100 °C, the viscous behavior prevails at low angular frequency, but a crossing point is reached, where the storage and the loss moduli meet (Table 3), in a similar way to the sol-gel transition observed for polymeric systems and

for other CNTs-IL dispersions [35], but this behavior cannot be visible at 25 °C. The inclusion of MWCNTs in [EMIM][DCA] scarcely changes the behavior of the ionic liquid, and very similar values of G' and G'' are found in these two samples. On the contrary, the addition of aligned-MWCNTs and SWCNTs in the ionic liquids shows a different scenario. Fluids with storage modulus G' higher than the loss modulus G'' are obtained, and the influence of increasing frequencies is much lower than in the case of [EMIM][DCA] and [EMIM][DCA]+MWCNTs. This observation would be in agreement with the presence of ordered nanostructures as it is also observed in the data above. The stronger structure is formed when SWCNTs are added to [EMIM][DCA].

Table 3. Crossover frequency and moduli values.

Fluid	ω (rad/s)	$G' = G''$ (Pa)
[EMIM][DCA] (25 °C)	17.8	2.7
[EMIM][DCA] (100 °C)	10.8	0.78
[EMIM][DCA] + MWCNTs (100 °C)	12.6	0.78

In the case of the CNTs dispersions, the Cox-Merz rule was tested but regrettably none of the samples showed a satisfactory superposition of steady-state viscosity and complex viscosity. This empirical rule states that for linear viscoelastic materials the magnitude of the complex viscosity is the same as the steady-state viscosity at equal values of frequency and shear rate. It has been shown to apply successfully for a number of polymer melts, homogeneous solutions, and also in polymer-ILs systems [49,50], but with relative success for aggregating systems. CNTs are known to have a tendency to aggregate and this could be the reason why these dispersions do not follow the Cox-Merz rule.

CONCLUSIONS

New dispersions of different types of 1 weight percent carbon nanotubes in the room-temperature ionic liquid 1-ethyl-3-methylimidazolium dicyanamide have been obtained. [EMIM][DCA] is able to disperse different types of CNTs. Raman spectroscopy results are in agreement with the existence of interactions between the ionic liquid molecules and the carbon nanotubes, and with a reduction of the nanotube-nanotube interactions.

The neat ionic liquid presents Newtonian behavior, but the addition of carbon nanotubes results in interesting Non-Newtonian fluids. The highest viscosity increase is observed for the dispersion of Single-Walled Carbon Nanotubes, followed by aligned Multi-Walled Carbon Nanotubes and Multi-Walled Carbon Nanotubes. The dispersion containing Single-Walled Carbon Nanotubes shows shear thinning effect, while aligned Multi-Walled Carbon Nanotubes in [EMIM][DCA] present shear thickening effect. In contrast, non-aligned Multi-Walled Carbon Nanotubes reach a Newtonian plateau under high shear. With the exception of Single-Walled Carbon Nanotubes, the viscosity-temperature behavior of the nanofluids correlates well with the Arrhenius model. For dispersions with Single-Walled Carbon Nanotubes and aligned Multi-Walled Carbon Nanotubes, under oscillatory frequencies, the storage modulus remains higher than the loss modulus for a wide range of frequencies. This is in agreement with a highly ordered structure for these nanotube morphologies, which is not observed for the more disordered non-aligned Multi-Walled Carbon Nanotubes. The Cox-Merz rule can be applied to [EMIM][DCA], but not to the dispersions with any of the Carbon Nanotubes used in this research.

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