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# **Rheological Behavior of Multi-Walled Carbon Nanotube- Imidazolium Tosylate Ionic Liquid Dispersions.**

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## **ABSTRACT**

The rheological behavior of 1-ethyl-3-methylimidazolium tosylate (EMIMTsO) and its dispersions with aligned and non-aligned multi-walled carbon nanotubes (MWCNTs) has been studied. Raman spectroscopy analysis has been carried out to characterize the samples. The effects of concentration, type of CNTs and temperature on the viscoelastic behavior of EMIMTsO have been evaluated. Regardless the concentration and type of added CNTs, a non-Newtonian behavior of the fluids has been found under shear stress. The ionic liquid and the EMIMTsO-MWCNTs 1 wt% dispersion showed a temperature-induced gelation. However, the addition of small concentrations of MWCNTs prevents from the formation of gels.

**Keywords:** Ionic liquids, rheology, shear flow, carbon nanotubes

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## **INTRODUCTION**

Ionic liquids (ILs) are molten salts at room temperature [1] which are generally formed by a combination of organic cations with organic and inorganic anions. Due to their unique properties such as negligible vapor pressure, large liquidus range, high thermal stability and ionic conductivity [2], these salts have attracted a growing interest in the fields of materials science and engineering [3-6]. In the recent years, the combination of ILs and oils with several types of nanophases has given rise to new nanostructured dispersions, with promising engineering applications [7]. Among available nanomaterials, carbon nanostructures such as nanotubes showed promising results as additives in lubricant oils, due to the weak van de Waals forces between the sliding surfaces [8]. In particular, multi-walled carbon nanotubes (MWCNTs) have been widely used in solid lubrication [9,10] and as lubricant additives [11,12]. Previous research has demonstrated that MWCNTs are well dispersed in an imidazolium-based IL and the resulting dispersion shows an excellent tribological performance [13].

Carbon nanotubes (CNTs) are known to be well dispersed in ILs and the resulting dispersions are stable and homogeneous, giving rise to new hybrid nanomaterials with exceptional properties and potential applications in a wide range of technological fields [14-16]. Fukushima et al. have 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 [14,17,18]. There are several mechanisms of interaction between CNTs and ILs which can act in parallel. Some authors have demonstrated that ILs interact with

CNTs through cation- $\pi$  and  $\pi$ - $\pi$  interactions [19,20] and there are some evidences revealing weak van der Waals interaction without an obvious influence of the electronic structure of CNTs [21]. Moreover, it has been recently proved via X-ray diffraction and molecular dynamics simulations that ILs can be encapsulated inside CNTs and not only on the external surface [22,23].

In recent years, the rheological characterization of ionic liquids has invoked a strong interest in the scientific community since this is one of the principal features to be taken into account for tribological applications [24,25]. In a Newtonian flow, shear stress is proportional to shear rate [26] and the viscous behavior is not affected by shear rate. In the case of fluids with a certain degree of phase ordering, the non-Newtonian phenomenon is typically prevalent [27]. Shear thinning of ILs has been reported previously in the literature because of the existence of liquid phase aggregates or networks [24,28,29]. This non-Newtonian behavior has been ascribed to molecular layering in the case of imidazolium-based ILs [30,31].

To the best of our knowledge, the rheological study of MWCNTs-ILs dispersions has not been attempted at the present. In this work, we present a rheological characterization of mixtures of two different types of MWCNTs in 1-ethyl-3-methylimidazolium tosylate (EMIMTsO). The shear effect on EMIMTsO-MWCNTs dispersions at different temperatures has been studied. Studies have been carried out for two different MWCNT concentrations in IL. Therefore, the effects of shear, temperature, type of CNTs and concentration are evaluated.

## **MATERIALS AND METHODS**

Multi-Walled Carbon-Nanotubes (MWCNTs) were purchased from Nanostructured and Amorphous Materials, Inc. (Texas, USA). Two different sets of nanotubes were used. The first one is a sample of MWCNTs with an external diameter of 8 nm and length of 0.5-2  $\mu\text{m}$ , with a purity of 95% and reference number 1225YJS. Aligned nanotubes were used as well, with an external diameter of 10-20 nm and a length of 5-15  $\mu\text{m}$ , with a purity of 95% and reference number 1215NMGA. In figure 1, transmission electron microscopy (TEM) micrographs of the commercial non-aligned (a) and aligned (b) MWCNTs are shown. It is important to notice that not only the aligned MWCNTs are larger than the non-aligned but also present a more highly ordered nanostructure. These TEM images were obtained with a high resolution JEOL JEM 2100 microscope.

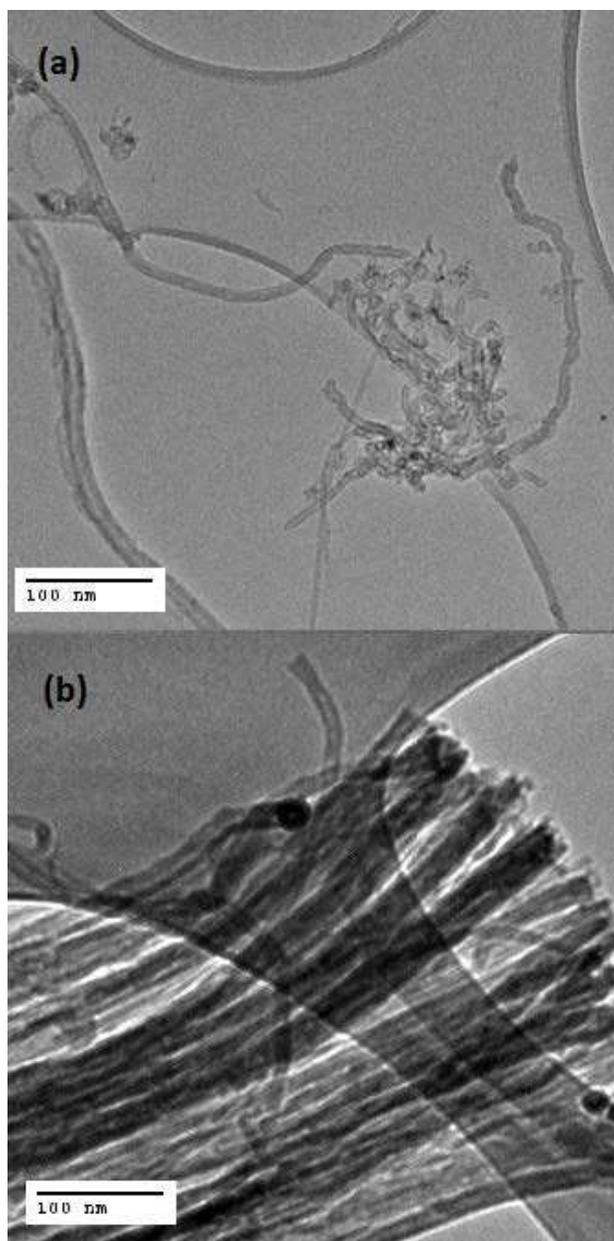
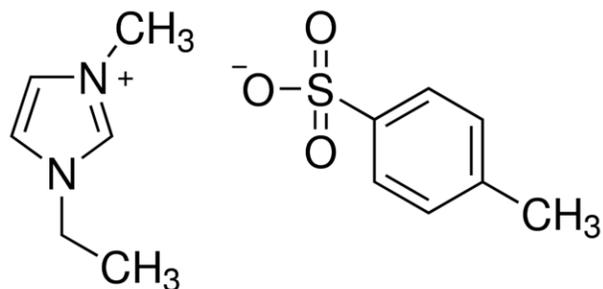


Figure 1. TEM pictures of non-aligned (a) and aligned (b) multi-walled carbon nanotubes.

The ionic liquid 1-ethyl-3-methylimidazolium tosylate (EMIMTsO) was purchased from Sigma-Aldrich with a purity  $> 98\%$ . The chemical structure of the ionic liquid is shown in the scheme 1.



Scheme 1. Chemical structure of 1-ethyl-3-methylimidazolium tosylate.

The procedure for the elaboration of EMIMTsO+MWCNTs dispersions consisted in the addition of MWCNTs to the ionic liquid in a 1 wt% proportion following the method described previously in [17] and also carried out in our earlier works [13,32]. The materials are weighed and mixed in an agate mortar and the resulting dispersion is manually blended for 10 minutes. The amount of material obtained each time is approximately 4 g. As a result, a concentrated suspension of EMIMTsO+MWCNTs is obtained with the appearance of a viscous black fluid (figure 2a). From this point, this fluid will be labeled as concentrated dispersion. In order to obtain the diluted dispersions, these concentrated mixtures are centrifugated at 4000 rpm for 1 hour. As it can be seen in figure 2b, precipitation occurs after centrifugation and a black precipitate appears at the bottom of the vial and a yellowish suspension (darker than the pure ionic liquid) is present in the upper part. The precipitate is composed by ionic liquid-modified MWCNTs which has been previously described [32] as additive to improve the tribological performance of polymers. The determination of the concentration of MWCNTs in the supernatant was attempted by means of thermogravimetric analysis, X-ray diffraction, infrared and visible spectroscopy, and differential scanning calorimetry, but the sensitivity of the methods was not high enough to give a good estimation and the

differences between the spectra obtained for the neat ionic liquid and the diluted dispersions were negligible. In summary, the influence of the concentration of MWCNTs in a concentrated regime of 1 wt% and a diluted regime with traces of MWCNTs will be evaluated.

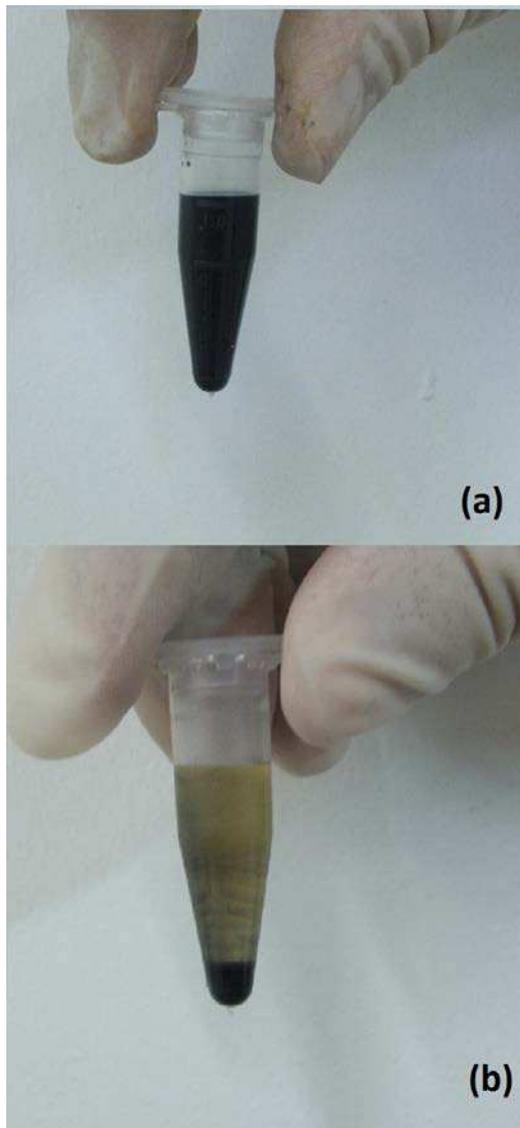


Figure 2. Concentrated (a) and diluted (b) dispersions of EMIMTsO with MWCNTs.

Raman analysis at room temperature was carried out using a Renishaw (Gloucestershire, UK) InVia microscope - spectrometer system. The spectrometer has a spectral resolution

of  $1 \text{ cm}^{-1}$  and a lateral resolution of 800 nm. Raman spectra were acquired with a Leica x50 objective with a numerical aperture (NA) of 0.75 in a backscattering configuration. A 785 nm diode laser dealing 170 mW on the sample at maximum power was used in this work. All experiments were performed using low power intensities (below 0.1 mW), to ensure no damage was inflicted to the samples. Intensities and wavenumber for the characteristic features were obtained by fitting peaks with Lorentzian-Gaussian functions. At least three spectra were taken for each specimen.

The rheological behavior of pure ionic liquid and the EMIMTsO+MWCNTs dispersions was determined 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 60 mm and a gap between plates of 1000 microns. Temperature was controlled by a Peltier system with an accuracy of 0.1 °C. Three different series of experiments were performed: shear flow curves, temperature ramps at a constant shear flow and oscillation. The shear flow influence on the viscosity was studied at 25, 50, 75 and 100 °C by increasing the shear rate from  $10^{-3}$  to  $500 \text{ s}^{-1}$  for a total period of time of 15 minutes. A series of experiments at 0.1, 1, 10 and  $100 \text{ s}^{-1}$  was performed confirming that our samples had reached the steady-state. To study the thermal effect on the viscosity, temperature ramps from 25 to 100°C with a speed of 1 °C/min were performed at a constant shear rate of  $50 \text{ s}^{-1}$ . Finally, oscillation experiments were performed employing a frequency range from 0.1 to 200 rad/s after setting the strain value of 0.2% to evaluate the behavior of the loss and storage moduli.

## RESULTS AND DISCUSSION

### Raman spectroscopy.

Figure 3 depicts Raman spectra obtained for the ionic liquid and its concentrated dispersions for both non-aligned MWCNTs (figure 3a) and aligned MWCNTs (figure 3b). Spectra have been normalized with respect to maximum intensity peaks. Plots have been shifted for clarity. D, G and D' bands are encountered in plots corresponding to MWCNTs and concentrated dispersions, both non-aligned and aligned MWCNTs. However, none of these bands are present in the diluted dispersions spectra, being these identical to the ionic liquid one. To obtain  $I_D$ ,  $I_G$ ,  $I_{G'}$  ratios in concentrated dispersions plots, pure ionic liquid spectrum was subtracted, to remove the contribution of the tosylate benzene ring C=C band centered at  $1600\text{ cm}^{-1}$  from carbon nanotubes G band.

MWCNTs show the characteristic G band at  $1592\text{ cm}^{-1}$ , assigned to the in-plane vibrations of the graphitic walls, the D band at  $1308\text{ cm}^{-1}$  originating from disorder in the graphitic structure, and the G' band, a second order feature of the D band, at  $2600\text{ cm}^{-1}$ , which is the result of a double resonance process, so it is more prevalent in high-purity MWCNTs [33]. The  $I_G/I_D$  intensity ratio is used as an indicator of the degree of crystallinity and purity of carbon nanotubes [34]. In table I a  $\Delta\omega\approx 4\text{ cm}^{-1}$  shift in the D and G peaks and a  $\Delta\omega\approx 10\text{ cm}^{-1}$  shift in the G' peaks are observed for both short and aligned MWCNTs in concentrated dispersions with respect to the pristine MWCNTs. These shifts might be due to  $\pi$ -cation interactions between nanotubes and ionic liquids [35]. The variations in the  $I_G/I_D$ ,  $I_{G'}/I_D$  and  $I_{G'}/I_G$  ratios are not statistically meaningful, which indicate that MWCNTs suffer no major chemical or structural changes when interacting with ILs.

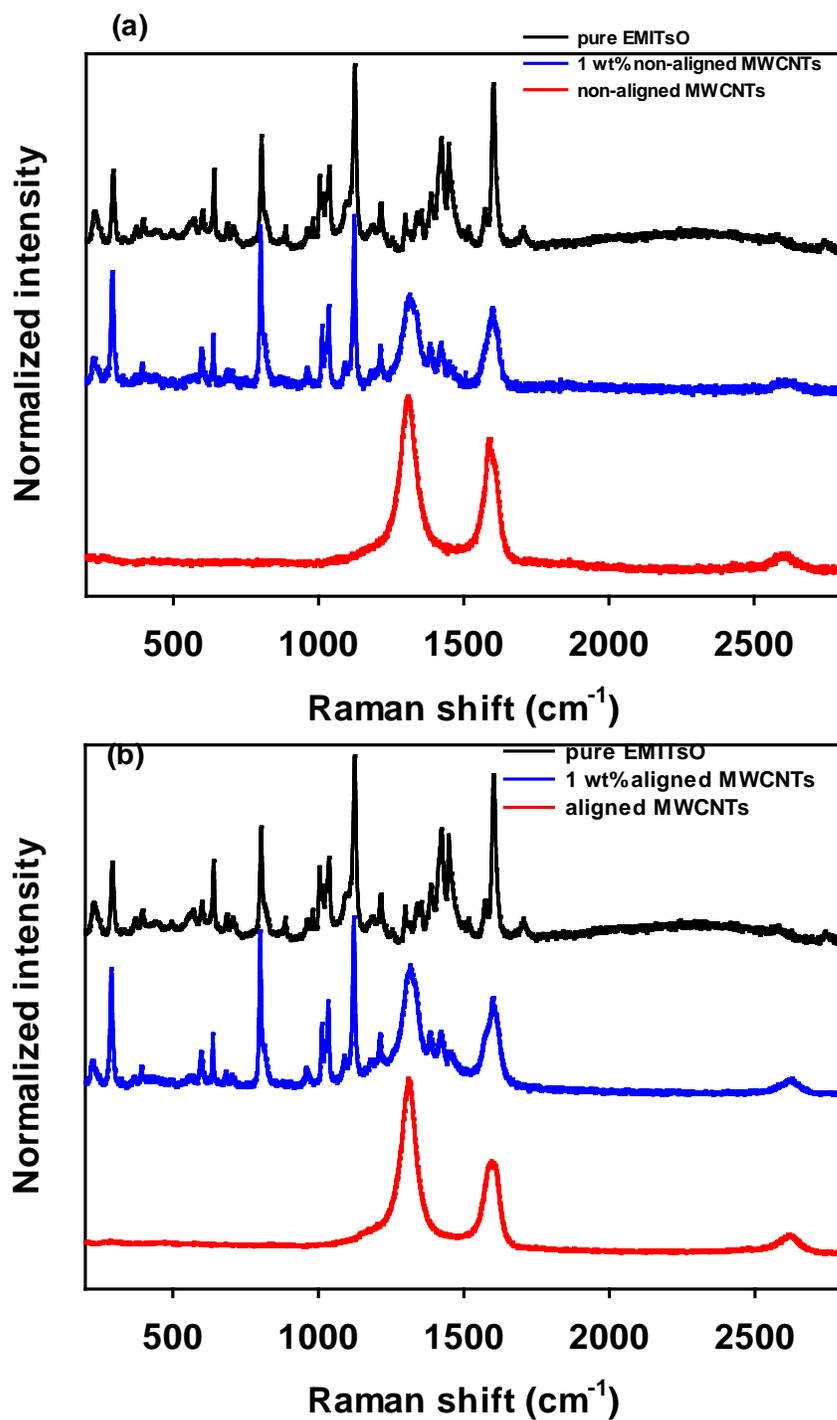


Figure 3. Raman spectroscopy of carbon nanotubes, ionic liquid and 1 wt% dispersions: (a) non-aligned MWCNTs and (b) aligned MWCNTs.

Table I. Intensity ratios and wavenumbers of D, G and G' bands for MWCNTs and its concentrated dispersions. Values in parentheses indicate standard deviation.

	non-aligned MWCNT	concentrated dispersion	aligned MWCNT	concentrated dispersion
$I_G/I_D$	0.52 (0.02)	0.44 (0.06)	0.40 (0.01)	0.45 (0.01)
$I_G/I_D$	0.13 (0.01)	0.18 (0.07)	0.13 (0.01)	0.16 (0.02)
$I_G/I_G$	0.25 (0.02)	0.42 (0.15)	0.33 (0.03)	0.35 (0.04)
$\omega_D$ (cm <sup>-1</sup> )	1307.2 (0.3)	1311.6 (0.3)	1308.5 (0.1)	1312.7 (0.3)
$\omega_G$ (cm <sup>-1</sup> )	1591.5 (0.4)	1595.7 (1.6)	1593.6 (0.1)	1596.5 (0.6)
$\omega_{G'}$ (cm <sup>-1</sup> )	2599.9 (1.4)	2610.9 (4.3)	2612.4 (0.8)	2621.1 (0.3)

### Shear flow.

The viscosity values of pure EMIMTsO under varying shear rates at 25, 50, 75 and 100 °C are depicted in figure 4. When shear is applied, this viscous system exhibits shear thinning behavior. A strong decay at low shear rate values can be appreciated at every temperature. Ionic interactions are present in the fluid leading to highly ordered structures in the absence of any kind of perturbation. However, these interactions between molecules are disrupted by the applied flow and a transition to a less ordered state might happen [24] and a decrease of viscosity is seen.

Two different regions are observed for pure EMIMTsO under shear. Firstly, a dramatic decrease of the viscosity is observed at very low shear rate (from 10<sup>-3</sup> s<sup>-1</sup> to 1 s<sup>-1</sup>) from approximately 7 to 0.7 Pa·s at 25 °C. This shear thinning region has been previously seen in other imidazolium-based ionic liquids studies [21,29,36,37] and has also been predicted by Molecular Dynamics simulations [38]. After this value is reached, at medium and high velocity rates, a Newtonian behavior is found and the viscosity is

constant with a value 10 times lower than the one found at low shear rate. At this point, the remaining intermolecular interactions are strong enough to resist the action of shear. Time effects were checked out with a backwards flow ramp performed in analogous conditions, i.e. the range of shear rate was set from 500 to  $10^{-3} \text{ s}^{-1}$  in 15 minutes. The differences between the absolute values of viscosity from backward ramp to forward ramp were negligible. Therefore, a total reversibility of the shear action can be considered to happen and only non-bonding interactions might be disrupted by the flow. An analogous behavior is found when temperature is increased up to 100 °C. A shear thinning region appears at low shear rate and a Newtonian plateau is reached circa  $1 \text{ s}^{-1}$  shear rate. However, the viscosity values at high shear rate have better reliability. As it is expected, the viscosity values of the ionic liquid decrease with temperature. The bonding of the molecules in EMIMTsO are easily disrupted with temperature because of the weak hydrogen [39] and electrostatic [40] interactions between the ion pair. In figure 4 it can be seen that, at 25 °C, the viscosity at high shear rate is approximately 1 Pa·s and this value decreases 100 times at 100 °C. Therefore, the rheological behavior of this kind of systems shows a strong dependency with temperature. Analogous experiences have been performed for dispersions of EMIMTsO with two different types of CNTs: non-aligned MWCNTs with a diameter of 8 nm and longer and aligned MWCNTs with a diameter of 20 nm. In both cases, the diluted and concentrated regimes of CNTs were evaluated at 25, 50, 75, and 100 °C.

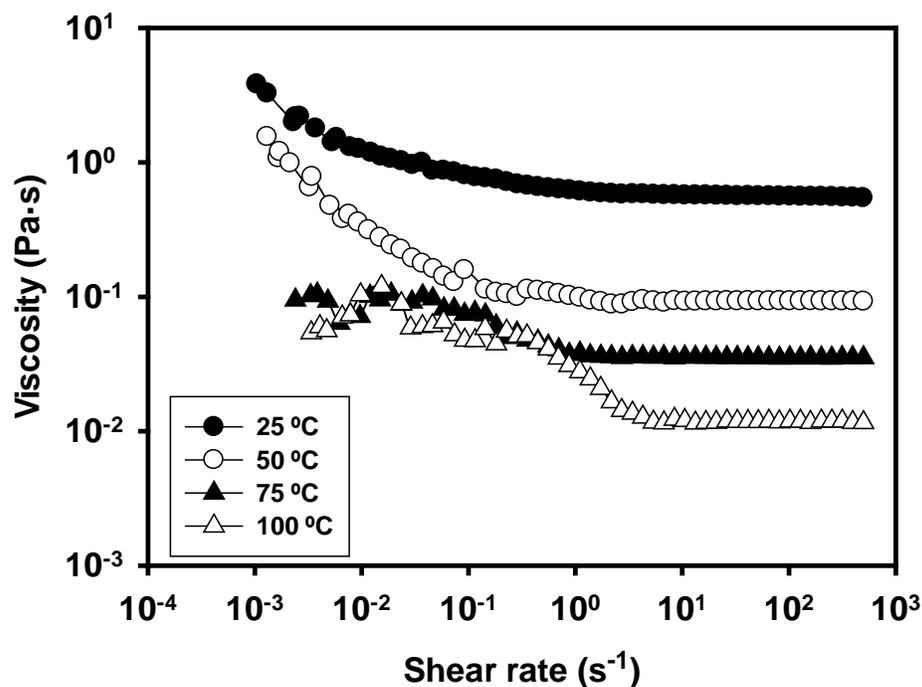
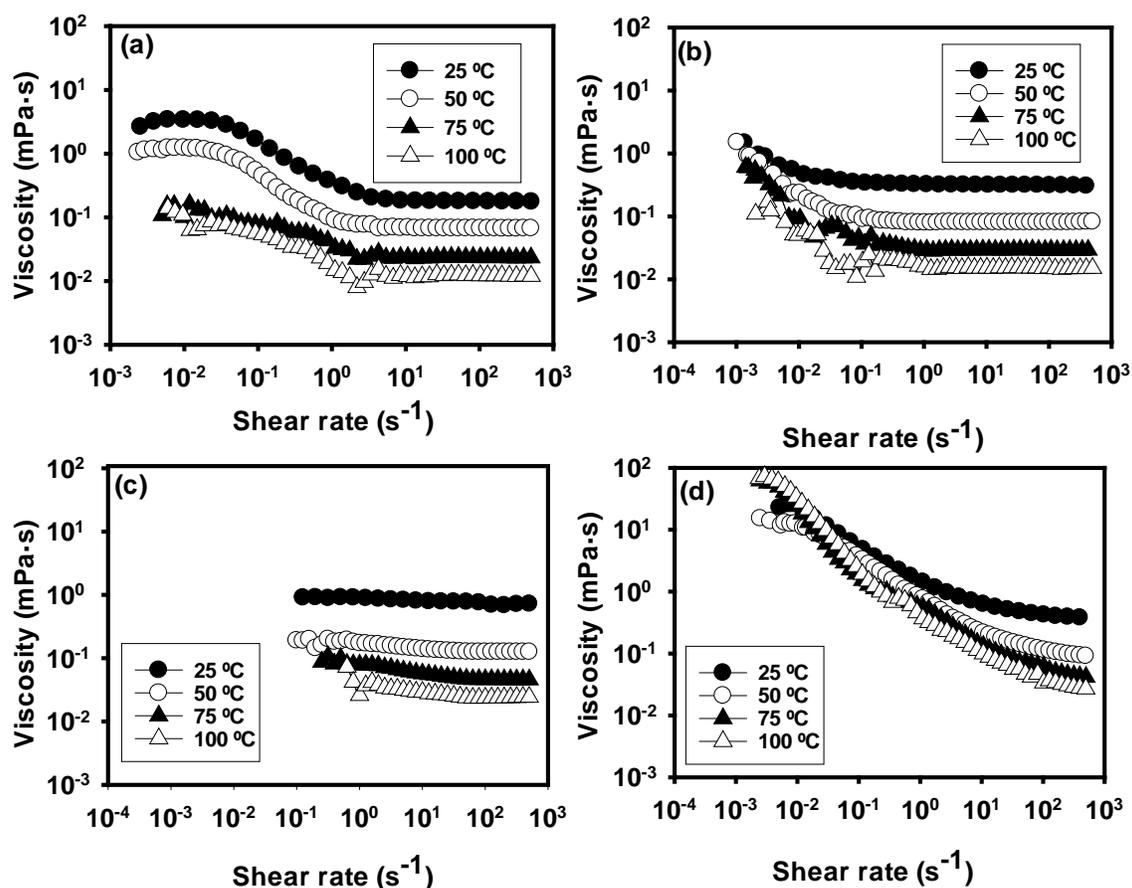


Figure 4. Viscosity behavior under variable shear rate for pure EMIMTsO at different temperatures.

For the diluted suspension of non-aligned MWCNTs in EMIMTsO (figure 5a), a Newtonian plateau is found at low values of shear rate. CNTs have a strong interaction with ionic liquids providing a higher ordered structure. Therefore, the resistance to flow will be higher than for pure ionic liquids and the viscosity is increased. However, in the case of aligned MWCNTs (figure 5b) this Newtonian plateau is not observed at low shear rates, indicating that the morphology of CNTs highly affects the order of the ions in the ionic liquid at low shear rate. In both cases, a shear thinning region appears when the shear rate is raised because of the disruption of intermolecular interactions and finally a Newtonian region can be observed at high speed.



**Figure 5.** Shear flow dependence of diluted non-aligned MWCNTs (a) and aligned MWCNTs (b), and concentrated dispersions of non-aligned MWCNTs(c) and aligned MWCNTs (d) at several temperatures.

It is interesting to point out that at high shear rates the viscosity values of both dilute dispersions are lower than the values found for EMIMTsO, as it is shown in Table II. Our hypothesis is that MWCNTs can be oriented in the direction of the flow and the resistance to flow is decreased because of the directional nature of shear flow. A similar behavior is observed when inclusion of fibers in non-Newtonian fluids results in a shear thinning effect. Fibers are oriented in the direction of the flow and the viscous behavior is hampered resulting in a decrease of viscosity [41]. Besides, imidazolium-based cations

have a great attraction to carbon nanophases [14], and then the interaction between the cation and the anion is suppressed and the anion has a higher mobility [42]. In our case, the presence of low quantities of MWCNTs may disrupt the interaction between the ions and the resulting dispersion shows a lower resistance to flow, as it will be further explained in the following sections. This effect seems to be decreased by the action of temperature and at 100 °C the values of viscosity are similar.

Table II. Values of viscosity in mPa·s at high shear rate extracted from figures 4, 5a and 5b.

Temperature (°C)	EMIMTsO	EMIMTsO + non-aligned MWCNTs	EMIMTsO + aligned MWCNTs
25	0.546	0.178	0.302
50	0.093	0.069	0.084
75	0.035	0.024	0.030
100	0.012	0.012	0.016

The behavior of the concentrated dispersions of EMIMTsO-MWCNTs is also depicted in Figures 5c (non-aligned CNTs) and 5d (aligned CNTs). The shear thinning regions are observed at low shear rate values. However, for the case of non-aligned MWCNTs the results were not reproducible under  $0.1 \text{ s}^{-1}$ . In contrast to the behavior described above, these systems are more viscous than pure ionic liquid in the whole shear rate range, especially when aligned MWCNTs are added. Therefore, the concentration of MWCNTs

in ionic liquids dispersions is a critical aspect to take into account in the viscous behavior under shear rate. A high concentration of nanotubes must lead to stronger interactions with EMIMTsO. Hence, more ordered structures are formed and the resistance to flow is higher. An interesting difference from the pure ionic liquid and the diluted dispersion is the absence of a Newtonian plateau at high speed. In the case of the non-aligned nanotubes, the decrease of viscosity is lower and it seems that a closely Newtonian behavior must happen for higher shear rates, but still a constant value is not completely reached at  $500 \text{ s}^{-1}$ . This behavior is more clear for the aligned MWCNTs concentrated dispersions in figure 5d. The total disruption of the structure does not occur at high shear rates, so a stronger structure should be present in this case.

### **Temperature effect.**

We have seen that temperature is a crucial factor to be taken into account for lubricants since arising severe tribological conditions, may result in saturation of the shear stress [43]. We have evaluated the influence of temperature on pure ionic liquid and on the diluted dispersions in figure 6. At a constant shear rate value of  $50 \text{ s}^{-1}$ , it can be seen in figures 4, 5a and 5b that these samples exhibit a Newtonian behavior. Thus, we performed a temperature ramp experiment from 25 to 100 °C at this set value of shear rate to evaluate the viscosity evolution. Experiments with the concentrated suspensions were attempted, with low reproducibility of the data, probably due to the non-Newtonian behavior of the samples.

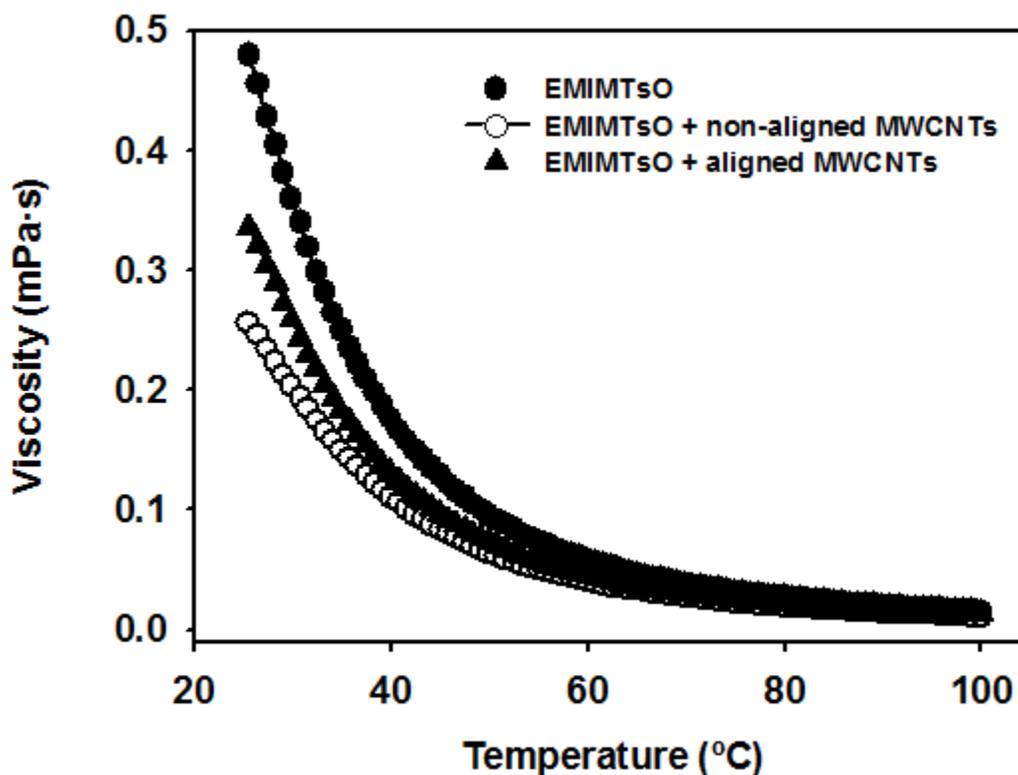


Figure 6. Effect of temperature on viscosity for EMIMTsO and the diluted EMIMTsO-MWCNT suspensions at a value of  $50 \text{ s}^{-1}$  shear rate.

According to the data shown in figure 6, the viscosity decreases with temperature for all our samples. Furthermore, the pure ionic liquid presents the highest values of viscosity and the sample with the lowest viscosity is the diluted dispersion of aligned MWCNTs in EMIMTsO. Since the temperature dependency presents an exponential-like decay, to take into account the overall temperature effect at this high shear rate, these data have been fitted to an Arrhenius equation [40] as follows:

$$\eta = \eta_0 \exp[E_a/RT] \quad (1),$$

where  $\eta$  is the viscosity,  $\eta_0$  a pre-exponential factor,  $E_a$  is the activation energy of the flow and  $R$  is the ideal gases universal constant. The values extracted from this fitting are shown in Table III. The higher value of the activation energy belongs to the pure ionic liquid and the lower value is given by the non-aligned MWCNT-EMIMTsO dispersion. Therefore, the addition of MWCNTs in a dilute regime enhances the capacity of the dispersion to flow compared to the pure ionic liquid. This is in agreement with the better fluidity seen in the flow curves in figures 5a and 5b. These higher values of  $E_a$  imply that EMIMTsO is more dependent on the effect of temperature than its diluted dispersions with MWCNTs and presents a higher resistance to flow as it has been seen above. These results could anticipate a good lubricating performance for the diluted MWCNT/IL dispersions.

Table III. Values of  $E_a$  and  $\eta_0$  for EMIMTsO, and diluted EMIMTsO+MWCNT dispersions.

	EMIMTsO	EMIMTsO + non-aligned MWCNTs	EMIMTsO + aligned MWCNT
$E_a$ (kJ/mol)	41.8	38.6	40.2
$\eta_0$ (Pa·s) $\times 10^9$	10.8	29.5	18.6

### Oscillation.

A series of oscillation experiments at different temperatures for pure ionic liquid and MWCNTs dispersions in EMIMTsO has been performed. In figure 7, the influence of the frequency on the storage modulus,  $G'$ , and the loss modulus,  $G''$ , of pure EMIMTsO values are depicted at several temperatures. When the frequency is increased, the storage

and loss moduli increase but in different manners. In figure 7a, we can observe that  $G''$  shows a potential growth with the frequency, while  $G'$  firstly keeps constant and finally there is a rapid increase from  $10^{-4}$  to 1 Pa at 25 °C. A similar trend can be seen if temperature is raised to 50, 75 and 100 °C. At low temperature (figures 7a and 7b), the viscous behavior prevails over the elasticity of the sample and  $G''$  is higher than  $G'$ . From this log-log plot, we can observe that at 25 °C  $(dG''/df) = 0.99$  and  $(dG''/df) = 2.15$ , meaning a typical flow response of the fluid [31]. A similar behavior is seen at 50 °C as well. On the contrary, two cross-over of the two moduli happens and sol-gel transitions are observed at 75 and 100 °C in figures 7c and 7d. At these high temperatures the values of the slope of  $G'$  are 1.05 and 1.00 at 75 and 100 °C, respectively, at low shear. But a crossing point occurs at approximately 20 Hz as frequency value at 75 °C (figure 7c), and 10 Hz at 100 °C (figure 7d). We also observe a deviation of the ideal value of 1 in the slope of  $G'$  when the gel point is reached. Therefore, a temperature-induced gel transition for pure ionic liquid is observed.

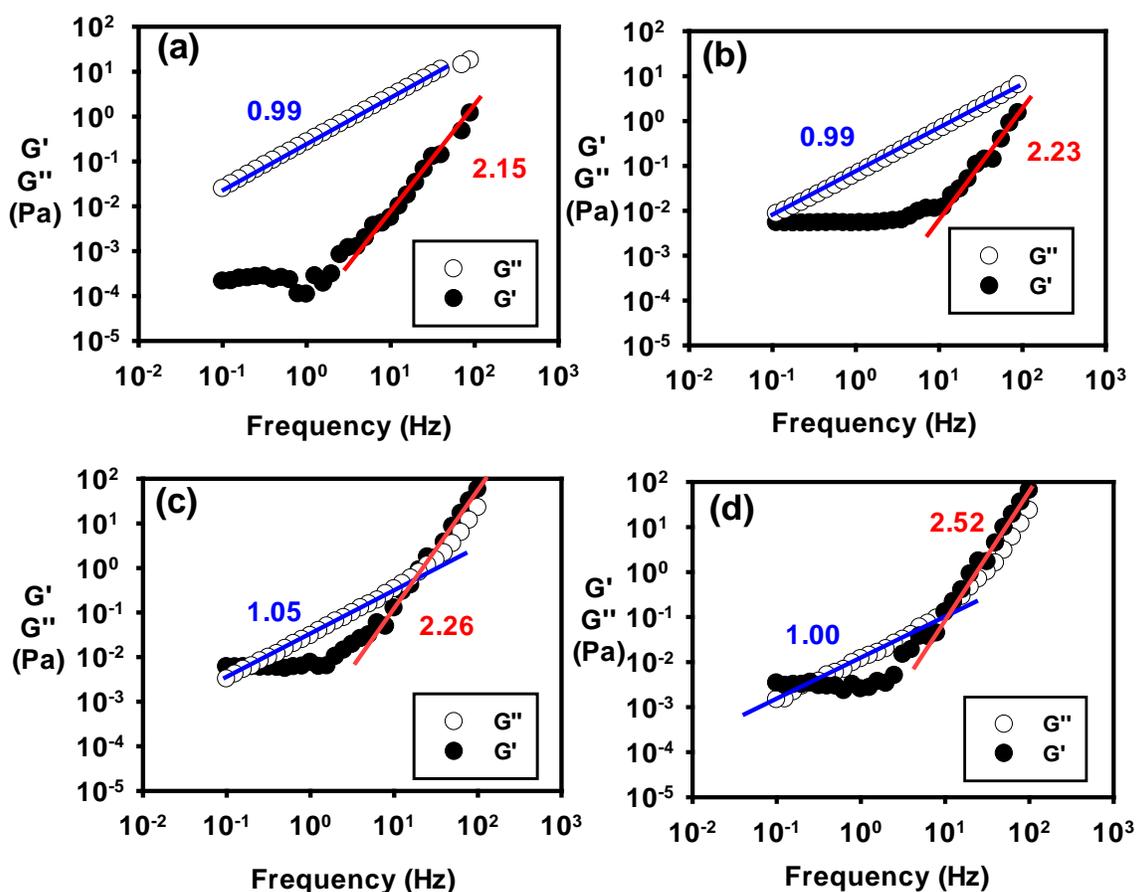


Figure 7.  $G'$  and  $G''$  of pure EMIMTsO at 25 °C (a), 50 °C (b), 75 °C (c), and 100 °C (d).

In figure 8 the analogous oscillation study for dispersed MWCNTs in EMIMTsO is plotted. Interestingly, when any kind of MWCNTs is added with low concentrations the loss modulus is predominant over the storage modulus all over the frequency range studied. Our samples follow a typical fluidic behavior with  $(dG''/df) \approx 1$  and  $(dG'/df) \approx 2$ . Then, the addition of low quantities of MWCNTs diminishes the values of  $G''$  and this effect is stronger for the aligned nanotubes. At high frequencies, the values of  $G'$  and  $G''$  seem to merge, similarly to the behavior observed in mixtures of low concentration of MWCNTs dispersed in melt polymers [44]. When temperature is raised, the values of loss modulus decrease, as seen for the pure ionic liquid. However, the values of the

storage modulus barely show a temperature effect. It is noteworthy that the presence of MWCNTs at low concentrations seems to avoid the temperature-induced gel transition seen for EMIMTsO at high temperatures (figures 7c and 7d). As it has been mentioned above, this can be interpreted as a breaking of the interactions between the ion pairs. A high affinity of imidazolium cations with carbon nanotubes has been previously reported [14,45-47], and the addition of low quantities of MWCNTs in EMIMTsO provokes an interaction between the cation and the nanotubes leading to a new structure which seems to be more mobile than the pure ionic liquid, because of a higher mobility of the tosylate, in agreement with the rheological data shown in tables II and III. Then, the inclusion of these low quantities of MWCNTs prevents from gel formation at high temperatures and a prevalent viscous behavior has been found.

On the other hand, when the concentrated dispersions of non-aligned MWCNTs are studied, the values of both  $G'$  and  $G''$  increase in comparison to the pure EMIMTsO, in agreement with shear rate dependence.  $G''$  is predominant over  $G'$  at low temperatures, but gel points can be only seen when the temperature is raised. These results could indicate that the presence of MWCNTs at high concentration promotes a more ordered structure and gels can be formed at lower temperatures in comparison to the pure ionic liquid. Besides, the crossing point and the deviation of the slope of  $G'$  to the value of 1 occurs at lower frequencies.

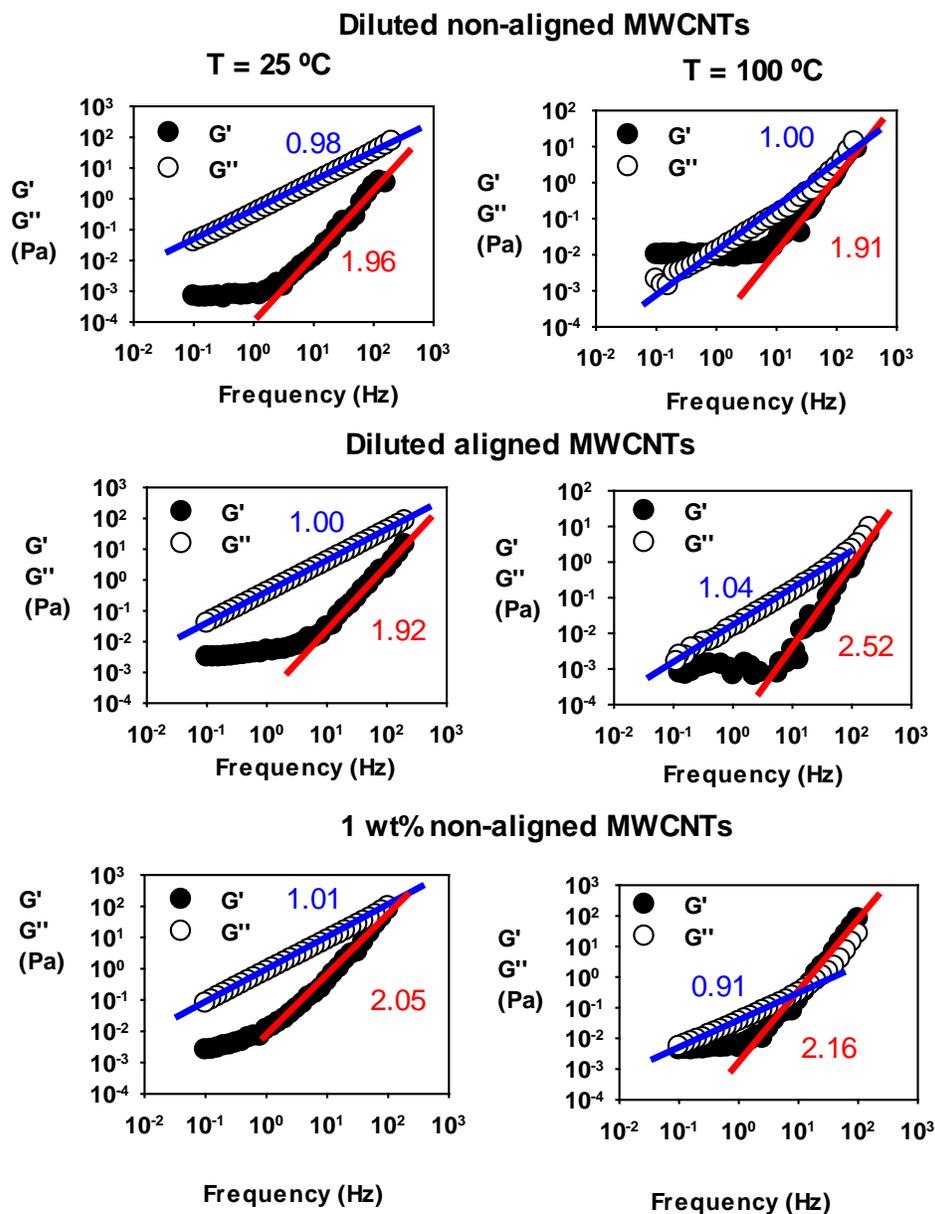


Figure 8. Loss and storage moduli of EMIMTsO-MWCNTs dispersions at 25 and 100 °C.

Figure 9 shows the influence of the addition of 1 wt% aligned MWCNTs to EMIMTsO on the loss and storage moduli at different temperatures. As it can be seen, this kind of CNTs dramatically enhances the formation of a gel. Although the presence of this additive increases the values of both  $G'$  and  $G''$  at room temperature, a gel point is not

seen, showing a similar behavior to the dispersions studied above. However, when the temperature is raised some differences appear. At 50 °C, a cross point can be observed probably due to the presence of a more organized structure in comparison with the other samples. Furthermore, at higher temperatures (75 and 100 °C)  $G'$  is always lower than  $G''$ . Thus, a temperature-induced gel formation might occur probably due to the development of an ordered nanostructure [48,49]. Then, the concentration effect is clear for this type of CNTs. At the low concentration studied above, the carbon nanotubes seem to disrupt the structure of the EMIMTsO, but at 1 wt%, a different scenario emerges. The concentration of CNTs in the dispersion is high enough to form a three-dimensional ordered structure leading to the formation of a gel, as seen for the non-aligned MWCNTs. Regarding the kind of CNTs studied, our hypothesis is that a higher alignment in the carbon nanotubes promotes the formation of stronger networks. These findings are in agreement with the Raman spectroscopy and TEM results, where the spectra and images showed more ordered structures in the aligned MWCNTs than in the non-aligned MWCNTs.

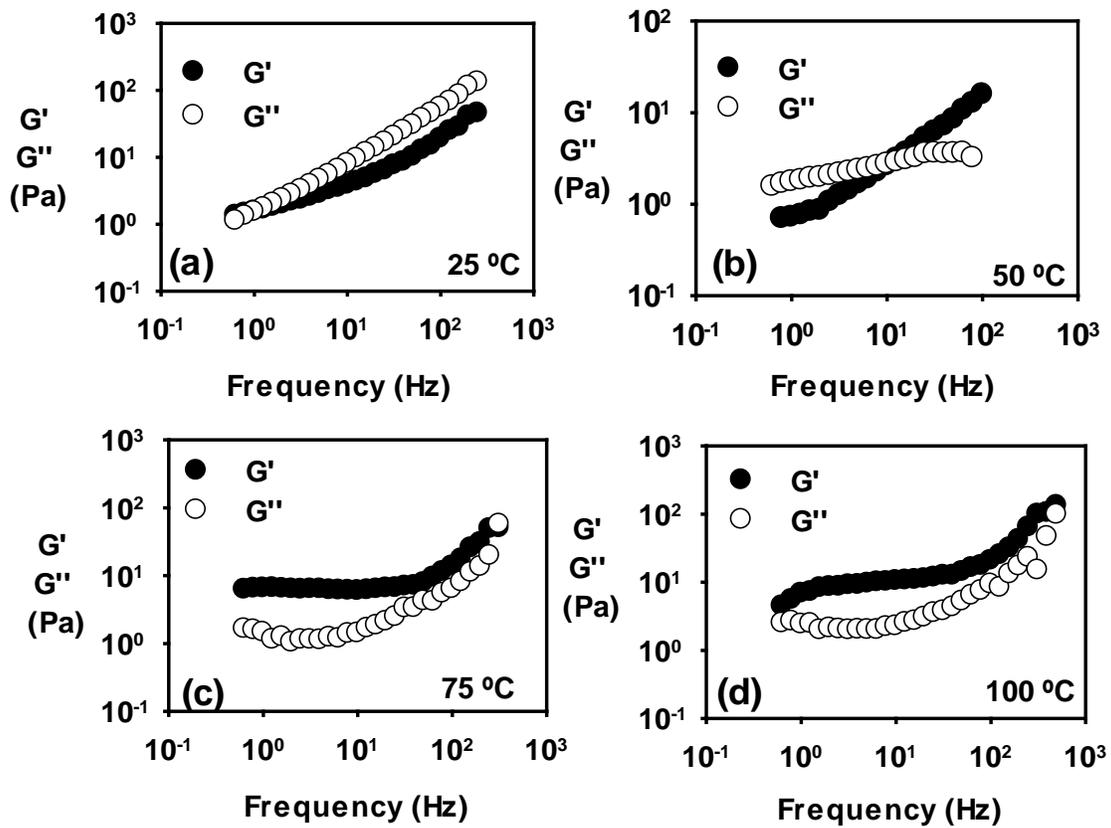


Figure 9. Loss and storage moduli of concentrated dispersions of aligned MWCNTs dispersions at 25 (a), 50(b), 75 (c) and 100 °C (d).

## CONCLUSIONS

The effect of temperature, concentration and type of MWCNTs on the viscosity of the EMIMTsO ionic liquid has been evaluated by rheological measurements. All samples showed a non-Newtonian shear thinning behavior when a shear flow is applied. The addition of MWCNTs in diluted regime provokes a decrease on the viscosity at high flow values, but the concentrated dispersions always present a higher viscosity than the pure EMIMTsO. Aligned MWCNTs have a more pronounced effect on the viscosity than non-

aligned MWCNTs. According to an Arrhenius fitting, the ionic liquid presents a higher resistance to flow than the diluted dispersions at a constant shear rate of  $50 \text{ s}^{-1}$ . An evaluation of the viscoelastic behavior has been carried out by means of oscillation experiments. At room temperature all our samples presented values of loss modulus higher than storage modulus, with  $(dG''/df) \approx 1$  and  $(dG'/df) \approx 2$ , meaning a typical fluid behavior. Neither the pure ionic liquid nor the dispersions, present any cross value of the storage and loss moduli. Therefore, none of the samples showed a gel transition at room temperature. When temperature is raised, a temperature-induced gel formation is seen in pure ionic liquid and concentrated dispersions, with higher  $G'$  and  $G''$  values in the case of the aligned MWCNTs. However, these three-dimensional networks are not found in the diluted dispersions.

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