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**Covalent vs. non covalent chemical modification of multiwalled carbon nanotubes based-nanofluids: stability and thermal conductivity steadiness over temperature**

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**Abstract**

Thermal conductivity enhancement coupled to nanoparticle dispersion stability over time are the two main conflicting requirements to overcome to develop carbon nanomaterial-based nanofluids. Both covalent and non-covalent approaches, having their own advantages and disadvantages, are commonly used for carbon nanotube based nanofluids development. However, they are rarely compared regarding their impact on stability and thermal conductivity performances for the same kind of nanofluid. In this work, multiwalled carbon nanotubes have been chemically modified by both covalent and non-covalent functionalization. For the

covalent functionalization, a simple oxidation method is applied. It consists of refluxing the powdered MWCNTs in  $\text{H}_2\text{SO}_4/\text{HNO}_3$  at 5 M concentration. For the non-covalent approach, both an anionic (sodium dodecyl sulfate) and a non-ionic (Pluronic P123, comprising poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) in an alternating linear fashion, PEO-PPO-PEO) surfactants were employed at a concentration of 1 wt.%. Nanofluids were prepared with multiwalled carbon nanotubes at a fixed concentration of 0.2 wt.% for both chemical modification approaches. The oxidation reaction occurs without significant structure damaging as shown by transmission electron microscopy, Raman spectroscopy, Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. UV-visible spectrophotometry analysis shows a remarkable stability with temperature in the 293.15-303.15 K range over one-week and for a longer period of 49 days for all the three types of nanofluids. Their thermal conductivity has been investigated in the same temperature range. For all the three nanofluid series prepared with a fixed concentration of carbon nanomaterials, a thermal conductivity enhancement compared to that of the base fluid has been observed. The thermal conductivity evolution with temperature is different for each type of nanofluid. The covalently oxidized multiwalled carbon nanotube based nanofluids showed the better thermal conductivity enhancement steadiness (around 7 %) with temperature. The discussion on the surfactant-based nanofluid behavior proposes the possible involved mechanisms as temperature increases for each surfactant.

## 1. Introduction

In recent years, with the exponential increase of energy consumption and the rise in energy price, thermal management has become an important issue for systems requiring efficient heat transfer. The current heat transfer fluids, generally deionized water (DIW), ethylene glycol (EG), mixtures of both, and oils, struggle to satisfy such demands. A possible solution is to use

heat transfer fluids with improved heat transfer features. Nanofluids consisting in conventional fluids (usually called based fluids) containing nanoparticles or nanomaterials have shown interesting thermal features capable to fulfill the requirements for efficient heat transfer [1]. Currently, it is expected that nanofluids with superior heat transfer features become a crucial part of renewable energy production systems like solar panels [2,3] or electronic devices [4] requiring high thermal transfer ability or dissipation rates. The nanofluid main idea is to disperse nanomaterials possessing high thermal intrinsic properties in a conventional base fluid in order to enhance the overall nanofluid thermal properties. Thus, if transferred efficiently, the higher the intrinsic thermal conductivity (TC) of the nanomaterial the better the nanofluid TC.

To preserve the intrinsic properties of nanoparticles during nanofluid process preparation is one of the main challenges in the nanofluid research field [5,6]. Achieving a good dispersion and stability of the nanomaterial in the base fluid is fundamental, otherwise agglomerates will jeopardize the further use of the nanofluid thermal properties. In that respect, a compromise must be achieved, as the engineered nanofluids must reach a compromise between maintaining the inherent TC of the nanomaterial while achieving an effective dispersion and stability within the base fluid. An intuitive thought would be to introduce larger quantities of nanoparticles into the nanofluid to boost their thermal features, however this strategy is counterproductive as, even if the nanofluid has to be stable, the resulting increased viscosity would require a substantial pumping power to promote the nanofluid flow within the cooling circuits [7,8]. In addition, high amounts of nanomaterials will also lead to the rise of the nanofluid production cost [9,10]. Hence, it is imperative to minimize the nanoparticle concentration during the nanofluid development while maintaining a good TC enhancement. Under these conditions, the effects diminishing the nanofluid TC transfer have to be controlled and limited.

Among the possible existing nanomaterials to prepare nanofluids, carbon based nanomaterials are interesting because they combine lightness and they are chemically inert [11]. Furthermore,

carbon nanotubes (CNTs) possessing remarkable TC values are ideal candidates for their integration in high performance nanofluids [12,13]. Unfortunately, pristine carbon nanomaterials, highly hydrophobic, do not well disperse in most polar liquids. Therefore, to achieve their proper dispersion, a chemical modification of their surface is essential [14]. The chemical modification or functionalization can follow either the covalent or the non-covalent approach. The non-covalent functionalization consists in adding surfactants to the nanofluids to promote the nanomaterial dispersibility in the base fluid [15]. This approach is widely used and often preferred to prepared CNT-based nanofluids thanks to its simplicity. Nevertheless, even if TC augmentations have been reported by the nanofluids prepared following the non-covalent approach, the presence of surfactants has as well some limitations: the non-thermally conductive surfactant layer surrounding the CNTs is responsible for lessening the nanofluid TC and they are additives with their own behavior which complicate the overall nanofluid system and show specific effects [7]. Covalent functionalization has as well proved to be able to reduce the carbon nanomaterial hydrophobicity by attaching hydrophilic functional groups on its surface [16]. Moreover, the covalent functionalization offers the opportunity to overperform carbon-based nanofluid TC without the presence of any additives. However, as the treatment is performed, it might cause a decrement of the CNT intrinsic properties due to the resulting structure damaging. Most of the studies indeed agree that increasing the amount of defects due to the covalent attachment of the functional groups directly hinders the carbon nanomaterial TC [17–19].

As today, literature counts with a high number of works studying many aspects of the carbon-based nanofluids. For the CNT-based nanofluid family, many studies and models have been developed to evaluate the effect of divers parameters on the resulting nanofluid TC, such as the CNT concentration [20] and the CNT aspect ratio [21]. Regarding the CNT functionalization type, researchers have already reported the influence of the surfactant quantity [22,23] and the

amount of induced defects in the nanotubes by chemical modification [24,25] on the nanofluid TC. The increase in concentration of surfactants in CNT based nanofluids and the increase in the amount of defects have been shown to negatively impact the nanofluid TC. The stability of covalent and non-covalent functionalized CNT-based nanofluids has also been investigated [26,27]. The impact of these two different types of chemical modification: *i.e.* covalent and non-covalent approaches, on the stability and the TC of the modified CNT-based nanofluids are most of the time studied separately and its evaluation by comparing both approaches for the same system is rarely studied in literature. Since carbon nanomaterials including CNT are complex nanomaterials, to determine in which extend the above-mentioned chemical modification can impact the CNT-based nanofluid behaviors and properties is still an open question.

In that regard, this study aims at analyzing, studying and comparing the efficiency of nanofluids prepared with covalently and non-covalently modified multiwalled CNTs (MWCNTs) and the effect of temperature on the nanofluid TC and stability. The performed covalent modification of the used MWCNTs has been selected based on a previous work focused on the optimization of the strength of the oxidation treatment, see ref. [24]. In this work, we had shown that by tuning the chemical modification of MWCNTs, it was possible to limit nanofluid TC decrease while keeping a good nanofluid stability. Here, the best-found compromise regarding the applied chemical modification has been applied to the MWCNTs and compared to the same MWCNTs stabilized by means of surfactants to prepare non-covalent MWCNT-based nanofluids. The MWCNTs were oxidized through an acid mixture (sulfuric/nitric) refluxing chemical treatment. The oxidized MWCNTs have been analyzed by transmission electron microscopy (TEM), Raman spectroscopy, Fourier transformed infra-red spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The oxidized MWCNTs served to prepare nanofluids using DIW as base fluid. For the non-covalent approach, two surfactants widely

recognized for their dispersive efficiency of carbon based nanomaterials [28,29], sodium dodecyl sulfate (SDS) and Pluronic P123 (P123), were employed for dispersing MWCNTs. Surfactants were dissolved at 1 wt.% in DIW and this mixture served as base fluid for the non-covalent approach. The starting MWCNT (untreated) were later added and dispersed to obtain the desired nanofluid. For all the prepared nanofluids in this work, the nanomaterial concentration was fixed at 0.2 wt.%, *i.e.* for the covalent approach 0.2 wt.% of the oxidized MWCNT was added to DIW (base fluid for the covalent approach) whereas for the non-covalent approach the starting MWCNT was added at 0.2 wt.% concentration to the mixture of surfactant/DIW (base fluid for the non-covalent approach) to obtain the desired nanofluid. The nanofluids TC features were characterized at different temperatures at 20, 30 and 40°C, respectively. Moreover, the stability of the dispersions was evaluated at these different temperatures and during two time periods (7 days and 49 days) with the help of ultra-violet visible (UV-Vis) spectrophotometry. Along with the result discussion, a mechanism is proposed regarding a possible surfactant reorganization phenomenon occurring within the nanofluid when the temperature is modified. The reported results revealing non-controlled behaviors over temperature when surfactants are used to help dispersion of MWCNTs in this study should boost the covalent approach for CNT-based nanofluids.

## **2. Materials and methods**

### **2.1 Materials**

The employed starting MWCNTs (sMWCNT) were synthesized by a chemical vapor deposition (CVD) process which took place at the Universiti Sains Malaysia facilities. As catalyst, Co-Mo and MgO were used. As purification treatment, the produced tubes were stirred in nitric acid at 60 °C for 30 min to remove the remaining catalyst components without introducing functional

groups. The resulting used MWCNTs possess 12 to 16 walls with an average diameter of 7 nm and have a length of around 10  $\mu\text{m}$  [30]. The starting used MWCNTs are referred to sMWCNT. For the oxidative treatments, sulfuric acid ( $\text{H}_2\text{SO}_4$ ), nitric acid ( $\text{HNO}_3$ ), hydrochloric acid ( $\text{HCl}$ ) and sodium hydroxide ( $\text{NaOH}$ ) were purchased from Sigma Aldrich and used as received. Sodium dodecyl sulfate (SDS) and Pluronic-P123 (P123) were purchased from Sigma Aldrich and employed at the desired amount for the nanofluid preparation.

## 2.2 Oxidative treatments

The oxidative treatment consisted of refluxing the starting MWCNTs with an acid mixture of  $\text{H}_2\text{SO}_4/\text{HNO}_3$  at 5 M concentration in a 1:1 volume proportion. Initially, 300 mL of the acid mixture were poured in a 500 mL round flask. Then, 300 mg of the departing sample were added. The flask was let to heat up at 110  $^\circ\text{C}$  in an oil bath and once the reflux started, it was let for 24 h. After, the flask was retired from the oil bath and set to cool down. Once room temperature (RT) was reached, the product was filtered and rinsed with DIW, then it was sonicated during 30 min in 150 mL of a  $\text{NaOH}$  solution at 4 M to eliminate potential carboxylated carbon fragments (CCFs) [31]. Later, the product was filtered and 250 mL of 2 M  $\text{HCl}$  were added. Finally, the chemically treated MWCNTs were rinsed with DIW until neutral pH was reached and set to dry with the help of a freeze-drier during 4 days. The resulting oxidized MWCNTs are named ox-MWCNT.

## 2.3 Nanofluid preparation

### 2.3.1 Sonication duration and surfactant concentration optimization

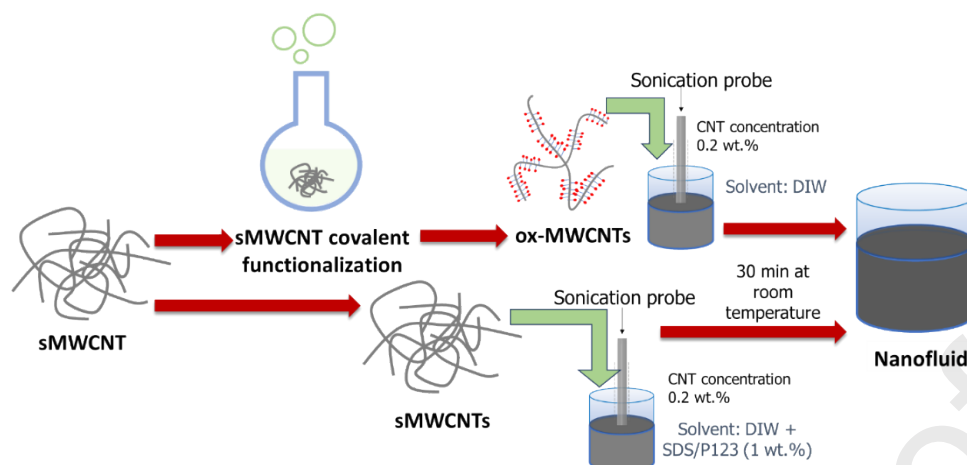
The sonication time for the 50 mL CNT-based nanofluids was optimized by increasing it step-by-step. The quality of the MWCNT dispersion just after sonication was checked with the coffee-ring method [32] after each 15 min of sonication cycle (not shown). An optimized duration of 30 min has been finally chosen. Regarding the surfactant concentration, the selection of the best concentration was based on optical microscopy (OM) observations *via* an



Olympus TH4-200 BXS1 optical microscope using the x10 objective. A rough estimation of the effect of the surfactant concentration was performed by a sampling (4 mL samples) approach and the coffee-ring effect method[32] (Supporting Information, Figure S1). The concentrations of Pluronic P123 (P123) and sodium dodecyl sulfate (SDS) were 0.25 (C1), 0.5 (C2), 1 (C3) and 2 wt.% (C4) and three different sonication durations: 2 (U1) , 4 (U2) and 8 (U3) min using a sonication probe (Sonics Vibra-Cell VCX750 equipped with a CV334 probe).

### **2.3.2 Nanofluid preparation with the optimized conditions**

Nanofluids were prepared with 0.2 wt.% of the starting MWCNTs for the non-covalent approach and 0.2 wt. % of the treated MWCNT in the case of the covalent approach (sMWCNT and ox-MWCNT, respectively). For the non-covalent approach, 1 wt.% of SDS or Pluronic P123 was used. For sake of reproducibility, each sample was prepared at least three times. For the oxidized MWCNTs, DIW, without any additive or surfactant, was used as base fluid. The base fluid for the nanofluids prepared following the non-covalent approach was the surfactant (Pluronic P123 or SDS)/DIW mixture. In all cases the MWCNTs were dispersed in the base fluid with the help of a sonication probe (Sonics Vibra-Cell VCX750 equipped with a CV334 probe) during 30 min at RT in a cyclic mode (2 sec on, 1 sec off) at 300 W. To avoid heating and evaporation, the nanofluid container was put in ice bath during the sonication. The nanofluids prepared with the oxidized MWCNTs and the starting MWCNT with SDS and Pluronic P123 surfactants are named nf-ox-MWCNT, nf-SDS-MWCNT and nf-P123-MWCNT, respectively. The schematic in Figure 1 illustrates the procedure applied for the nanofluid preparation.



**Figure 1.** Schematic of the procedure employed to prepare the studied nanofluids with sMWCNT and ox-MWCNT. The surfactants were added to DIW during the dispersion step. The ox-MWCNT were first functionalized and then dispersed in the corresponding base fluid.

#### 2.4 MWCNT characterization after nanofluid preparation

Droplets of the oxidized MWCNTs after being submitted to sonication following the procedure described in section 2.3.2 have been deposited to a glass slice and let naturally dried before Raman spectroscopy analysis. Both Pluronic P123 and SDS based MWCNT nanofluids have been loaded in a vacuum filtration set-up equipped with a Merck Durapore PVDF (polyvinylidene difluoride) membranes of porosity of 5  $\mu\text{m}$  and washed three times with 200 mL of DIW. After drying, the MWCNTs were added to ethanol and roughly dispersed in a sonication bath for 5 min. A drop of the obtained dispersion was then deposited on a glass slice and naturally dried.

#### 2.5 MWCNT characterization methods

The TEM observations were performed using a JEOL JEM-ARM 200F Cold FEG apparatus equipped with a spherical aberration (Cs) probe corrector and working at an accelerating voltage of 80 kV. For the TEM grid preparation, first the starting and treated MWCNT were

dispersed in ethanol and gently sonicated in an ultrasonic bath during 5 min. A droplet of the prepared dispersion was placed on a TEM copper grid covered with a holey amorphous carbon film (200 mesh size) (Delta Microscopies). For the TEM figures, a selection of representative images was made from a batch of about 40 images.

Micro-Raman spectroscopy was carried out with a Jobin Yvon LabRAM HR800. The apparatus is equipped with a CCD detector cooled to  $-70\text{ }^{\circ}\text{C}$ . For the characterization performed here, a 633 nm wavelength laser was used as the incident beam focused on the sample with a microscope through a wide length x100 objective and a numerical aperture of 0.50. The powdered MWCNTs have been gently dispersed in ethanol in a sonication bath for 5 min and a drop of the solution was deposited on a glass slice and let naturally dried at ambient conditions before analysis. For each sample an average of 10 spectra were recorded from randomly selected locations. In each case, the spectrum background was subtracted and the maximum intensity of the D and the G bands served to calculate the D intensity over the G intensity ratio ( $I_D/I_G$ ). For the Raman figures, the spectrum being the closest to the average  $I_D/I_G$  was chosen to be show.

For FTIR analysis, a Nicolet 6700 FT-IR (Thermo Scientific) spectrometer in ATR mode (diamond crystal) was used. At least 5 spectra of each sample were recorded using 100 scans and a resolution of  $2\text{ cm}^{-1}$ .

A kratos Axis Ultra (Kratos Analytical, U.K.) spectrometer equipped with a monochromatic Al  $K\alpha$  source (1486.8 eV) was employed for the XP. Th spectra were obtained at a takeoff angle of  $90^{\circ}$  with a step size of 1.0 eV and an analyzer pass energy of 160eV. For the high resolution regions, a step size of a 0.1 eV and a pass energy of 20 eV were used.

## 2.6 Thermal conductivity measurements

The TC of base fluids and nanofluids were evaluated at least 10 times in the temperature range of 293.15 to 313.15 K with a THW-L2 device (Thermtest Inc., Richibucto Road, NB, Canada). The measurement is based on the transient short hot-wire method according to the ASTM D7896 standard. The experimental conditions and protocol previously considered in [33] were here followed. As indicated earlier [24], an average absolute deviation (AAD) around 1 % in the temperature range of 293.15 to 313.15 K has been reported for DW, in agreement with previous study by Prado *et al.* [34] considering similar experimental facility, fluid and temperatures.

## **2.7 Nanofluid stability investigation**

The UV–visible spectrophotometry characterization of the nanofluids has been carried out with a Varian Cary7000 spectrophotometer in the 200–700 nm range using quartz cuvettes (28-F/Q/10) with an optical path of 2 mm furnished by Jasco France. As commonly found for such absorptive materials [35–37], the nanofluids were first diluted at a ratio of 1:10 and the absorbance of the resulting dispersion was measured by using a double beam mode and deducting the absorbance of the base fluid served as reference. Sample relative absorbance was compared at 500 nm as usually reported in literature [38,39] and followed for a week and after 49 days. The estimated measurement error is of 2 %. The nanofluids were stored in a thermostatic bath (Corio C-B5) set at the desired temperature during the whole duration of the stability measurements.

## **3. Results and Discussion**

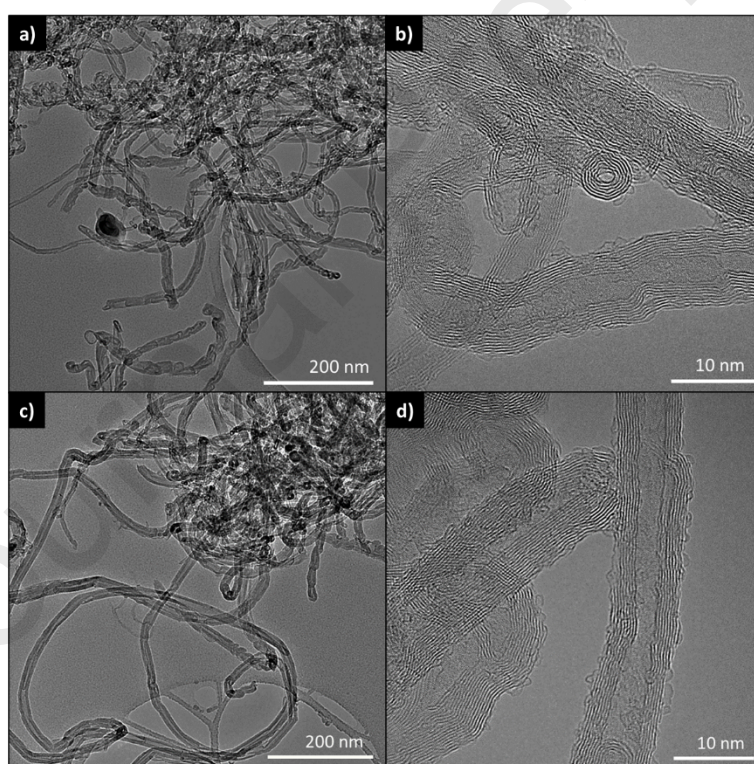
### **3.1 Chemical modification of the MWCNTs for optimizing nanofluid preparation**

#### **3.1.1 Morphological, structural and chemical study of the starting and oxidized**

#### **MWCNTs**

From complementary characterization techniques, the morphological structural, and chemical properties of the starting MWCNTs (sMWCNT) and the MWCNTs treated by the acid mixture of  $\text{H}_2\text{SO}_4/\text{HNO}_3$  at 5 M (ox-MWCNT) have been investigated by TEM, Raman spectroscopy, FTIR analysis and XPS respectively.

From TEM microscopy (Figure 2), for both the starting (Figures 2a and 2b) and the treated MWCNT, sMWCNT and ox-MWCNT, (Figures 2c and 2d) samples, their wall structure seems of similar quality. The observations of the functionalized MWCNTs by  $\text{H}_2\text{SO}_4/\text{HNO}_3$  at 5 M do not evidence any visible damaging evidencing that the applied treatment do not strongly attack the carbon network and avoids formation of breaks or holes in the oxidized MWCNT walls (Figures 2c and 2d).



**Figure 2.** Typical TEM micrographs of the starting MWCNTs (a & b) and oxidized MWCNTs by  $\text{H}_2\text{SO}_4/\text{HNO}_3$  at 5 M (c & d).

Raman spectroscopy provides valuable insights about carbon nanomaterials structural modifications introduced by a chemical treatment. The “G band” (approximately at  $1590\text{ cm}^{-1}$ ) arises from the vibrations in the  $sp^2$  network while the “D band” (around  $1330\text{ cm}^{-1}$ ) indicates the presence of disorders or defects in the  $sp^2$ -hybridized carbons. It is possible to obtain an asset of the carbon nanomaterial structural modification by comparing the parameter  $I_D/I_G$  before and after treatment. Furthermore, as the chemical treatment modifies the carbon hybridization from a  $sp^2$  state towards  $sp^3$  (defects) by the introduction of the oxygen containing groups, it is expected that the carbon network modification leads to an increase of  $I_D/I_G$  ratio from Raman spectra.  $I_D/I_G$  can be obtained by simply dividing both bands intensities (in this case the maximum intensity). The spectra of both the raw and the functionalized MWCNTs are shown in Figure 3a. The calculated  $I_D/I_G$  is  $1.20 (\pm 0.24)$  and  $1.56 (\pm 0.15)$  before and after being functionalized by  $\text{H}_2\text{SO}_4/\text{HNO}_3$  at 5 M, respectively. An increase of 30 % of  $I_D/I_G$  after the chemical treatment is hence observed, reflecting well the carbon network modification and indicating the presence of more defects in the ox-MWCNT structure.

The FTIR method, which principle is based on the bond vibration sensitivity, can be used to identify the functional groups present at the CNT surface. The spectra of the non-functionalized and the functionalized MWCNTs are shown in Figure 3b. As expected, the characteristic black bone (C=C) stretching vibration of the CNTs is visible in the starting and treated MWCNTs in the  $1560\text{-}1640$  domain [40]. Compared to the raw CNT spectrum, ox-MWCNT spectrum shows additional peaks attributed to C-O and C=O stretching detected in the  $1260\text{ - }1310\text{ cm}^{-1}$  range and in the  $1680\text{ - }1740\text{ cm}^{-1}$  range, respectively.

The XPS analysis serves as a semi-quantitative method to evaluate the C and O atomic environment and ratio in carbon-based nanomaterials. As the applied chemical treatment introduces O functions in the CNT structure, an increase in O amount is expected after functionalization. The calculated O/C ratio for the sMWCNT was of 3.4 % whereas for the ox-

MWCNT this value reached 9.4 %. The binding energy of the C1s of both sMWCNT and ox-MWCNT (Figures 3c and 3d, respectively) can be decomposed in several peaks depending on the carbon atom environment. Table1 and Table2 gathers the component contributions on the fitted C1s and O1s spectra respectively. Sample ox-MWCNT displays an increment in the C-O and C=O components, as it is displayed in Figure3d, the C-O and C=O contributions appear to be visually more pronounced. Moreover, this augmentation becomes more evident in Table1, where increments of around 60 and 80 % for C-O and C=O components are reported for ox-MWCNT. Regarding the O1s decomposition of sMWCNT (Figure 3e) and ox-MWCNT (Figure 3f), the last presents an augmentation in the O=C component. The augmentation is also reflected in Table 2, being of around 11 % for O=C.

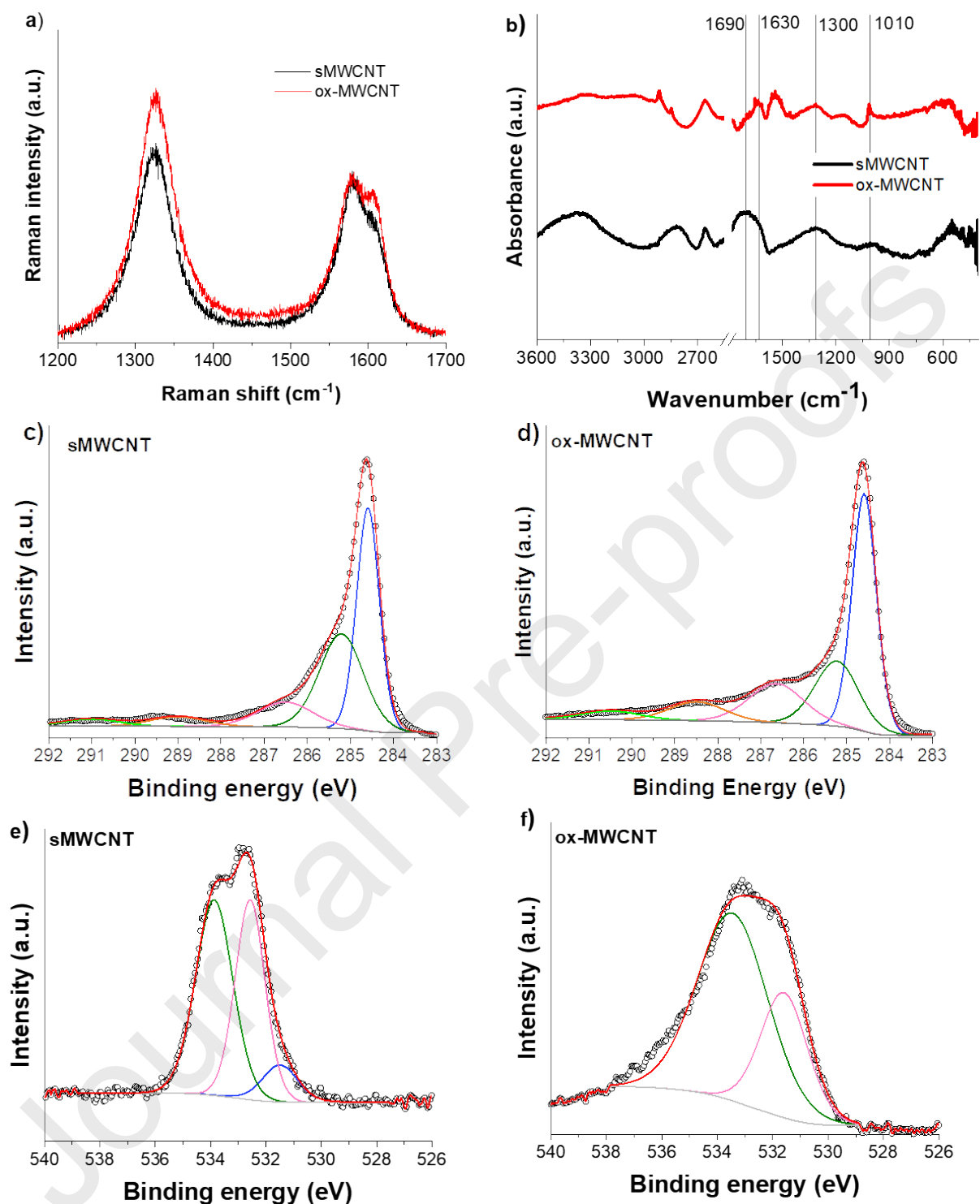
**Table 1.** Decomposition of XPS C1s of sMWCNT and ox-MWCNT. For each sample the component position (Pos.) (eV) and atomic concentration (Conc.) (%) are given. In the ox-MWCNT row, increment or decrement degree of each component compared to sMWCNT is given in %.

<b>Component concentrations of C1s</b>										
Contributions	C sp <sup>2</sup>		C sp <sup>3</sup> / C-H		C-O		C=O		$\pi$ - $\pi^*$	
	Pos. (eV)	Conc. (%)	Pos. (eV)	Conc. (%)	Pos. (eV)	Conc. (%)	Pos. (eV)	Conc. (%)	Pos. (eV)	Conc. (%)
<b>sMWCNT</b>	284.6	43.8	285.2	36.2	286.5	11.9	289.0	4.7	291.0	3.4
<b>ox-MWCNT</b>	284.6	43 (-2 %)	285.2	27 (-34%)	286.6	17.4 (+68 %)	288.5	8,5 (+80%)	290.6	4.1 (+20 %)

**Table 2.** Decomposition of XPS O1s of sMWCNT and ox-MWCNT. For each sample the component position (Pos.) (eV) and atomic concentration (Conc.) (%) are given. In the ox-MWCNT row, increment or decrement degree of each component compared to sMWCNT is given in %.

Sample	Component concentrations of O1s					
	O-M		O=C		O-C	
	Pos. (eV)	Conc. (%)	Pos. (eV)	Conc. (%)	Pos. (eV)	Conc. (%)
sMWCNT	531	2.1	532.6	27.5	534	70.4
ox-MWCNT	-	-	531.6	30.7 (+11 %)	533.4	69.3 (-1 %)





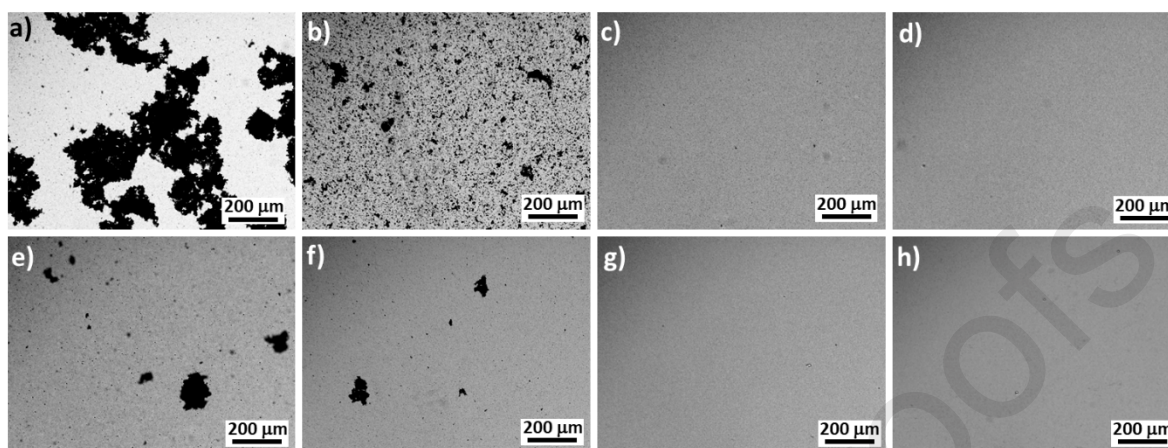
**Figure 3.** Raman spectra (a), FTIR spectra (b), XPS C1s decomposition and XPS O1s decomposition of the starting MWCNTs (sMWCNT) (c & e) and MWCNTs functionalized by H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> (ox-MWCNT) (d & f).

The found increase of  $I_D/I_G$  from Raman spectroscopy after the chemical treatment and the clear presence of oxygen-containing bonds in the oxidized MWCNTs from FTIR bring the evidence of the functionalization occurrence of the MWCNTs and the efficient grafting of oxygen-containing groups to their walls by refluxing them in the 5 M  $H_2SO_4/HNO_3$  mixture. Moreover, the increment in oxygen content found by XPS for ox-MWCNT sample which is undeniably related to the efficiency of the applied functionalization treatment is in agreement with the Raman spectroscopy results. The TEM observations which do not show any damaging on the MWCNT walls after their functionalization confirm the good preservation of their structure by the soft acid conditions used for the oxidation treatment in agreement with the limited increase of  $I_D/I_G$  ratio after the chemical treatment.

### **3.1.2 Optimization of the surfactant concentration**

The amount of surfactant in CNT-based nanofluids has to be minimized while guaranteeing a good dispersion quality of the CNTs in the base fluid. In this work, a sampling evaluation approach was conducted in order to optimize the surfactant concentration for both Pluronic P123 and SDS (Supporting Information, Figure S1). While maintaining the MWCNT concentration at 0.2 wt.% and the sonication time at the longest duration, the surfactant concentration was varied from 0.25 to 2 wt.%; typical investigated surfactant concentration range to achieve good dispersion ability [15].

The OM images of the MWCNT dispersions prepared with 0.25, 0.5, 1 and 2 wt.% of both Pluronic P123 and SDS are shown in Figure 4.



**Figure 4.** OM images of the MWCNT dispersions prepared with 0.2 wt.% of MWCNTs and the same sonication time of 8 min for a dispersion volume of 4 mL and different surfactant concentrations: Pluronic P123 at a) 0.25 wt.% (P123 C1U3), b) 0.5 wt.% (P123 C2U3), c) 1 wt.% (P123 C3U3) and d) 2 wt.% (P123 C4U3) and SDS at e) 0.25 wt.% (SDS C1U3), f) 0.5 wt.% (SDS C2U3), g) 1 wt.% (SDS C3U3) and h) 2 wt.% (SDS C4U3).

From the OM images, for both surfactants, it clearly appears that at low concentration of surfactants, the MWCNTs are still aggregated. When the concentration of Pluronic P123 and SDS was further increased to 1 and 2 wt.%, the OM images become more homogeneous and only a few small dark dots are visible, being the sign that high quality dispersions were achieved. For the preparation of the CNT-based nanofluid, the surfactant concentration of both Pluronic P123 and SDS of 1 wt.% was selected because it allows to meet the criteria of a good dispersion with a limited amount of surfactant.

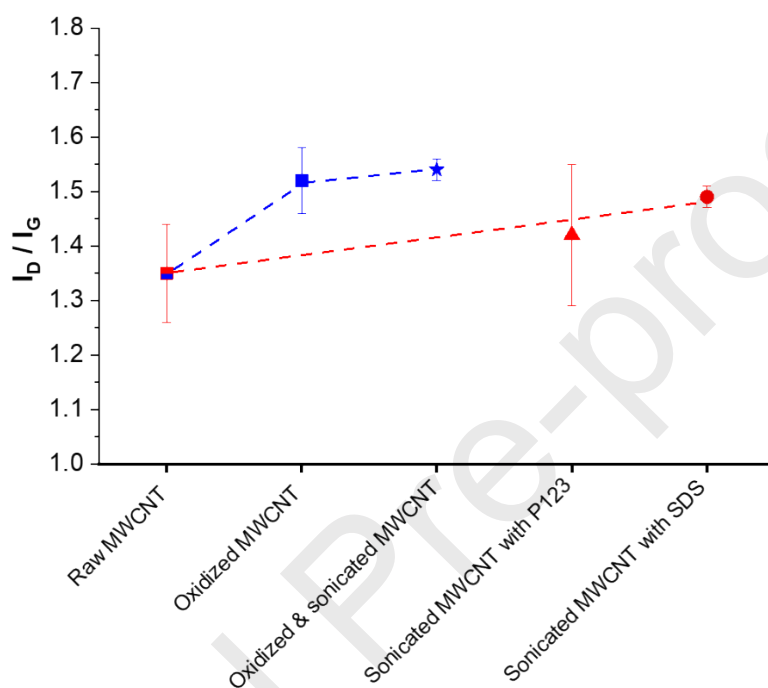
### 3.1.3 Damaging of the MWCNTs after nanofluid preparation

After putting into evidence the occurrence of functionalization with a limited introduction of defects and optimizing both the sonication time and the surfactant concentration, and before studying the stability of the chemically modified MWCNT nanofluids, a Raman spectroscopy investigation was conducted for the purpose of evaluating the possible introduction of defects into the MWCNT structure within the nanofluids through sonication for the 3 types of the used chemical modifications in this work, *i.e.* covalently functionalized MWCNTs (ox-MWCNT), Pluronic P123- and SDS non- covalently functionalized MWCNT (P123-MWCNT and SDS-MWCNT, respectively).

It is widely known that ultrasound waves which propagate in a liquid can induce a cavitation phenomenon [41,42]. This disruption of continuity in the liquid phase creates a considerable local pressure gradient which can damage the MWCNTs [43] and can have consequently dramatic impact on the physical properties including their TC and that of the corresponding nanofluids [44].

The MWCNTs have been studied by Raman spectroscopy after nanofluid preparation in order to evaluate their possible damaging after 30 min of sonication (cf. Experimental section).  $I_D/I_G$  ratios before and after nanofluid preparation for the three kinds of nanofluids is shown in Figure 5. The  $I_D/I_G$  ratio of the starting MWCNTs is of  $1.35 \pm 0.09$  in agreement with the value found in the section 3.1. In accordance with the preceding findings in section 3.1, after being oxidized, the  $I_D/I_G$  ratio of the chemically treated MWCNTs increased up to  $1.52 \pm 0.06$  due to introduction of oxygen functional groups in the MWCNT structure. After being submitted to sonication, their  $I_D/I_G$  ratio is of  $1.54 \pm 0.02$  and it has only slightly increased compared to before sonication meaning that the applied sonication procedure guarantee limited additional damaging due to possible cavitation or chemical attack effects [41,42]. Regarding the non-covalent approach with Pluronic P123 or SDS used to assist MWCNT dispersion in the base

fluids, the  $I_D/I_G$  is of  $1.42 \pm 0.13$  and  $1.49 \pm 0.02$ , respectively. Here again, the increase in  $I_D/I_G$  is not significant leading to a negligible additional defect number in the MWCNT structure due to sonication.



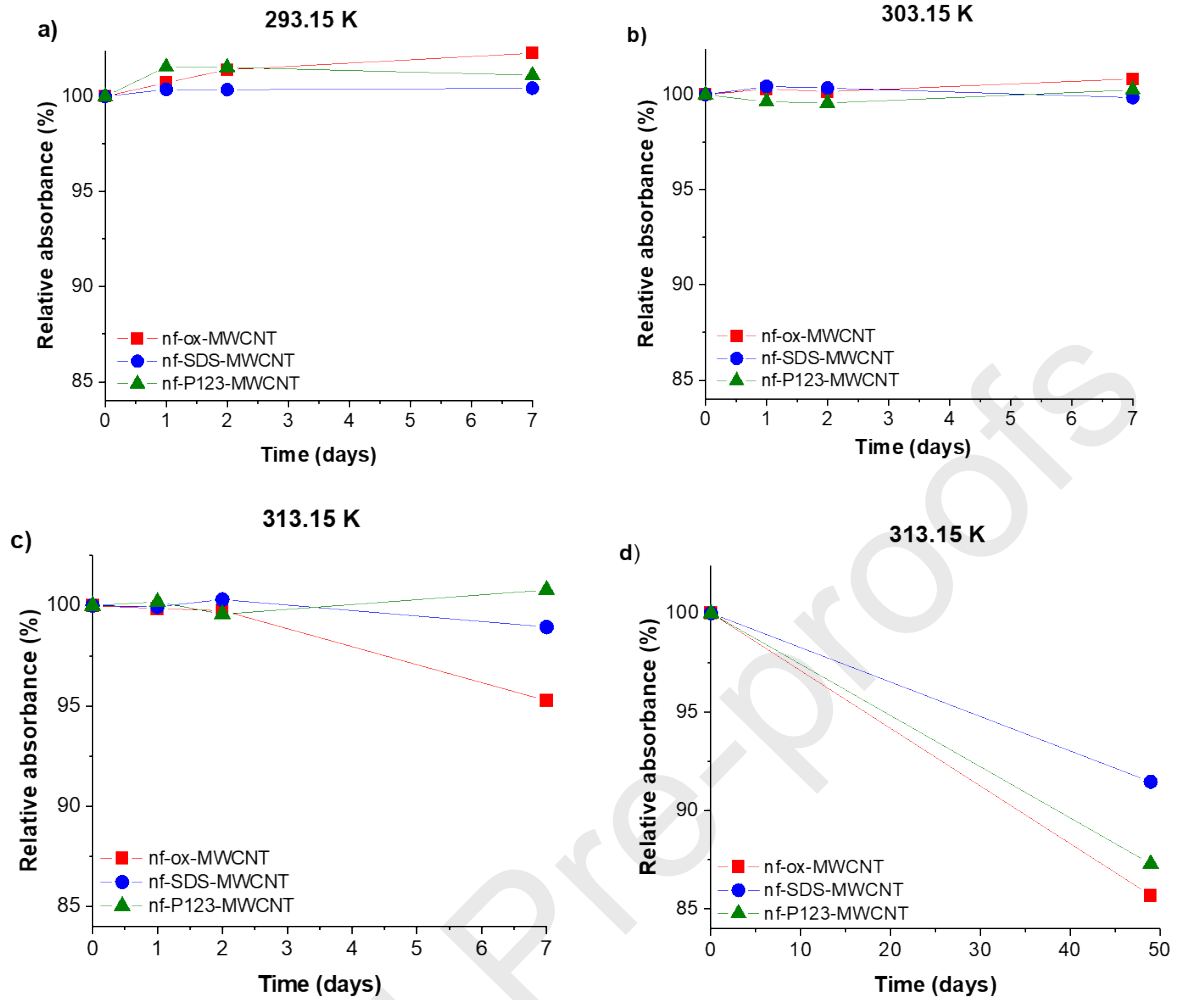
**Figure 5.**  $I_D/I_G$  of the starting and oxidized MWCNTs before and after nanofluid preparation by both the covalent and the non-covalent approach. The dash-point lines are guides for the eyes, the covalent and the non-covalent approach are in blue and in red, respectively.”

### 3.2 Covalent vs. non-covalent functionalization of MWCNTs for nanofluids

#### 3.2.1 Stability of the covalently and non-covalently functionalized MWCNT based nanofluids

The nanofluid stability was studied over time using UV-visible absorbance spectrophotometry. According to the Beer-Lambert law, the UV absorbance of a dispersion is directly proportional to its concentration. Typically, when destabilization occurs, carbon nanomaterials tend to

gradually aggregate and settle which will induce absorbance to diminish with time [45]. The relative nanofluid absorbance for the three prepared MWCNT-based nanofluids during a 7 days-period at temperatures of 293.15, 303.15 and 313.15 K and for a longer time (49 days) at 313.15 K is displayed in Figure 6, respectively. The relative absorbance decrease of both the covalently and non-covalently modified MWCNT-based nanofluids is less than 5 % after one week from UV-Visible spectrophotometry measurements (Figures 6a-6c). The highest observed decrease in absorbance intensity was found at 313.5 K for the covalently modified MWCNT-based nanofluid (nf-ox-MWCNT) after 7-day, this decay is limited to only 5 % of the initial absorbance (Figure 6c). When the measuring time was prolonged up to 49 days (separated experiment), the absorbance reduction (8-13 %) remains limited for both covalently and non-covalently modified MWCNT-based nanofluids (nf-ox-MWCNT, nf-SDS-MWCNT and nf-P123-MWCNT, respectively) (Figure 6d). The above stability investigation shows that the three proposed approaches to improve MWCNT dispersion and stability over time offer all a good efficiency.



**Figure 6.** Relative absorbance of the nanofluids prepared with the covalent and non-covalent modified: with MWCNTs oxidized by  $H_2SO_4/HNO_3$  (nf-ox-MWCNT) and with the starting MWCNTs dispersed with SDS (nf-SDS-MWCNT) and Pluronic P123 (nf-P123-MWCNT) during a 7 day-period at a) 293.15 K (20 °C), b) 303.15 K (30 °C), c) 313.15 K (40 °C) and during 49 days at d) 313.15 K (40 °C).

### 3.2.2 Thermal conductivity features of the covalent and non-covalent functionalized MWCNT based nanofluids

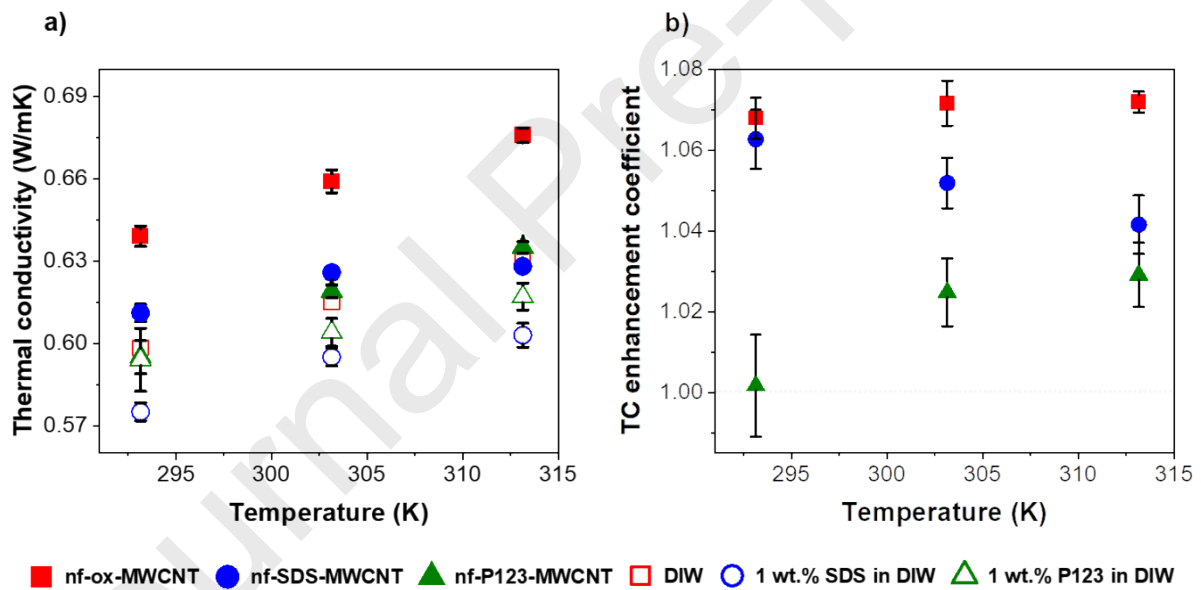
The TC enhancement coefficients ( $TC_{e\ coefficient}$ ) which evaluate the enhancement of the TC of the nanofluid compared to that of the used base fluid were calculated by dividing the measured nanofluid TC by that of the corresponding base fluid. In the case of the covalently

modified MWCNT-based nanofluid (nf-ox-MWCNT), the coefficient was obtained relative to DIW and in the case of the non-covalently modified MWCNT-based nanofluids (nf-SDS-MWCNT and nf-P123-MWCNT) the value was calculated relative to the surfactant (SDS or Pluronic P123 at 1 wt.)/DIW mixture. In both cases the Eq.(1) below was employed.

$$TC_e \text{ coefficient} = \frac{TC_{nf}}{TC_{bf}} \quad \text{Eq.(1)}$$

where  $TC_{nf}$  and  $TC_{bf}$  are the measured TC of the nanofluid and that of the respective base fluid.

The TC and the  $TC_e$  coefficient (calculated using Eq. 1) of the prepared nanofluids and that of their respective base fluids, measured at 293.15, 303.15 and 313.15 K are presented in Figure 7 and the corresponding reported values of TC can be found in in Table 3.



**Figure 7.** TC of nanofluids and the employed based fluids (a) and  $TC_e$  coefficients (b) at 293.15 K (20 °C), 303.15 K (30 °C) and 313.15 K (40 °C) prepared with the covalently modified MWCNT-based nanofluid by  $H_2SO_4/HNO_3$  (nf-ox-MWCNT) and the two non-covalently modified MWCNT-based nanofluids prepared with SDS (nf-SDS-MWCNT) and P123 (nf-P123-MWCNT).



**Table 3.** Covalently modified MWCNT-based nanofluid (nf-ox-MWCNT) and non-covalently modified MWCNT-based nanofluids (nf-SDS-MWCNT and nf-P123-MWCNT) and their corresponding base fluid measured thermal properties, including temperature of the measurement, thermal conductivity and thermal conductivity enhancement coefficient.

Temperature (K)	Thermal property	nf-ox-MWCNT		nf-SDS-MWCNT		nf-P123-MWCNT	
		nanomaterial	Base fluid	nanomaterial	Base fluid	nanomaterial	Base fluid
		ox-MWCNT	DIW	sMWCNT	DIW + SDS	sMWCNT	DIW + Pluronic P123
293.15	TC (W/mK)	0.639 (±0.004)	0.598 (±0.002)	0.611 (±0.003)	0.575 (±0.003)	0.595 (±0.006)	0.594 (±0.11)
	TC enhancement coefficient	1.068 (±0.006)		1.063 (±0.007)		1.002 (±0.012)	
303.15	TC (W/mK)	0.659 (±0.004)	0.615 (±0.002)	0.626 (±0.002)	0.595 (±0.003)	0.619 (±0.002)	0.604 (±0.005)
	TC enhancement coefficient	1.072 (±0.006)		1.052 (±0.006)		1.025 (±0.008)	
313.15	TC (W/mK)	0.676 (±0.002)	0.630 (±0.001)	0.628 (±0.002)	0.603 (±0.004)	0.635 (±0.002)	0.617 (±0.005)
	TC enhancement coefficient	1.072 (±0.003)		1.042 (±0.007)		1.029 (±0.008)	

Both the covalently and non-covalently functionalized MWCNT-based nanofluids show an increase in TC as temperature increases. This behavior is commonly observed for nanofluids [46,47]. For all the produced nanofluid types, the presence of the MWCNTs whatever the functionalization process, induces a TC enhancement compared to the respective base fluid; the TC enhancement for the P123 stabilized nanofluid is however limited at 293.15 K (Figure 7a and Table 3). Variations in  $TC_e$  coefficients with temperature reveal some differences between the three types of the prepared nanofluids (Figure 7b and Table 3). The nanofluid prepared with the covalently modified MWCNTs (nf-ox-MWCNT) shows a stable  $TC_e$  coefficient around +7 % over the studied temperature range. When a surfactant is used, SDS or Pluronic P123, a decrease in  $TC_e$  coefficient as a function of temperature in the case of SDS (nf-SDS-MWCNT) and an

increase in the case of Pluronic P123 (nf-P123-MWCNT) are observed for the respective non-covalent MWCNT-based nanofluids. These results reveal that the type of base fluid, in particular the presence of surfactant, has a great impact on the TC behavior as function of temperature.

The lack in constancy of  $TC_e$  coefficient in the case of the non-covalent approach can be due to modification of the rearrangement of the surfactant molecules occurring within the base fluid and consequently onto the MWCNT. It is known that SDS micelles are sensitive to temperature [48,49]. SDS micelle aggregation number (number of surfactant molecules per micelle) decreases with increasing temperature. That means that the colloidal equilibrium between the SDS molecules isolated in solution, those self-assembled in micelles and those adsorbed on the MWCNT surface is modified as temperature increases towards increasing the number of isolated SDS molecules in solution by desorption from micelles and MWCNT surface. Furthermore, it is reported that below the critical micelle concentration (CMC), TC decreases with concentration, *i.e.* with the number of isolated surfactant molecules in solution. In our case, the used SDS concentration for the MWCNT-based nanofluid (1 wt.%) is above the SDS CMC (0.22-0.25 wt.% [50]) in the temperature range investigated, TC increases with concentration [51]. Under these conditions, the number of isolated SDS molecules is expected to be higher within the nanofluid medium compared to the base fluid and  $TC_e$  coefficient consequently diminishes with temperature as it is observed for the SDS stabilized MWCNT-based nanofluids.

For the block copolymer non-ionic surfactants, like the PEG-PPO-PEG family or Pluronic P123, a different behaviour than that observed for ionic surfactants, like SDS, as a function of temperature has been reported. These polymer-based surfactant strongly adsorb on hydrophobic surfaces thanks to the PPO regions and they form a loop and a chain structure with the hydrophilic sections (PEG) rejected far from the MWCNT surface [52]. As a result, the

adsorption process is not reversible since the probability that all the PPO regions of the copolymer molecule desorb at the same time is very weak. Furthermore, dehydration of the PEG parts with temperature is responsible for reduction in size of the whole adsorbed copolymer layer on the MWCNT external walls. Such phenomenon may induce a facilitated thermal conduction for these block copolymer stabilized MWCNT-based nanofluids as temperature is increased and consequently a  $TC_e$  coefficient increasing with temperature, which could explain the behaviour observed for the Pluronic P123 non-covalently functionalized MWCNT-based nanofluids as temperature raises.

Regarding the thermal properties of the three prepared functionalized MWCNT-based nanofluids, at low temperature (293.15 K), the TC of the SDS stabilized MWCNT-based nanofluid almost reaches that of the covalently modified MWCNT-based nanofluid (Figure 7b and Table 3). As already mentioned, the MWCNT-based nanofluid prepared with P123 shows a very low  $TC_e$  coefficient compared to the two others at 293.15 K. As temperature increases, the use of SDS as surfactant induces a decrease in TC performances and the MWCNT-based nanofluid prepared with Pluronic P123 shows an improvement in TC with temperature. However,  $TC_e$  coefficient of this latter remains lower than that of the MWCNT-based nanofluid prepared by the covalent approach. We believe that the found constancy in TC performances as a function of temperature for the covalently modified MWCNT-based nanofluid can be considered as a real advantage for further applications, especially since the used temperature is often even higher in real conditions of nanofluid practical utilization.

#### 4. Conclusion

MWCNT-based nanofluids have been prepared from covalently and non-covalently modified MWCNTs. The used covalent approach led to a limitation of the structural quality damaging of the MWCNTs and at the meantime, has led to introduce a sufficient number of grafted oxygen-containing groups so that the stability of the corresponding nanofluids are shown to be quite stable over a long period of time up to 49 days. The MWCNT-based nanofluids prepared with SDS and Pluronic P123, an anionic and a non-ionic surfactant, respectively, have been observed to be as well stable during the same duration. The TC of all the three series of MWCNT-based nanofluids has been shown to be improved compared to that of the respective base fluid. The TC enhancement coefficients have revealed different behaviors as function of temperature for each type of nanofluid. The change in the TC enhancement coefficient for the surfactant stabilized MWCNT based nanofluids is explained by the modification of the surfactant organization itself at the MWCNT surface within the nanofluid with temperature. In the case of the covalently MWCNT water-based nanofluid, the related TC enhancement coefficient appeared quite stable as temperature varied. This study brings an evident advantage of the covalent strategy to develop MWCNT-based nanofluids reliable for their further use as heat transfer fluids. Each CNT type has its own chemical reactivity. In particular, it depends on its geometry, structure and amount of pre-existing defects. Even if, the variation in any of this parameter could have an impact on the material response to a chemical treatment, the main result of the present work which evidences a clear advantage of the covalent approach compared to the non-covalent one could be transferred to other kind of carbon nanomaterials, including CNTs and graphenes. Further works are however required in order to find the oxidation conditions depending on the kind of CNT used for nanofluid designing.

#### Author Contributions

Experiments, characterization, writing and data analysis: M.P.; TEM imaging and analysis: M.E.; spectroscopy characterization and analysis: S.H.; project administration and review and editing: A.R.M.; thermal conductivity experiments: S.G.; methodology, thermal conductivity experiments and analysis, review and editing: P.E.; supervision, project funding, data analyzing, methodology, writing, review and editing: B.V.

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### **Conflicts of interest**

The authors have no conflicts to declare.

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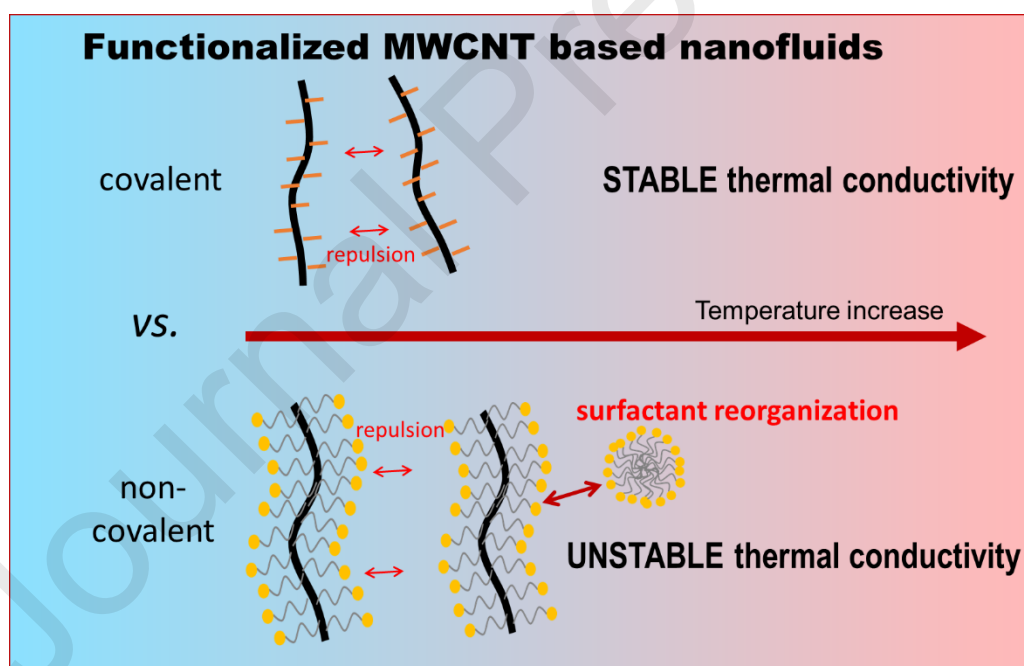
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**Covalent vs. non covalent chemical modification for multiwalled carbon nanotubes based-nanofluids: stability and thermal conductivity steadiness over temperature**

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**Graphical abstract**



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### Highlights

- Nanofluids based on MWCNTs chemically modified by both covalent and non-covalent functionalization
- Stability over time has been shown to be achieved for 49 days
- Different thermal conductivity behavior with temperature
- Surfactant reorganization with temperature forbids thermal conductivity stability

### Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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### **Author Contributions**

Experiments, characterization, writing and data analysis: M.P.; TEM imaging and analysis: M.E.; spectroscopy characterization and analysis: S.H.; project administration and review and editing: A.R.M.; thermal conductivity experiments: S.G.; methodology, thermal conductivity experiments and analysis, review and editing: P.E.; supervision, project funding, data analyzing, methodology, writing, review and editing: B.V.