Testing industrial laboratory dispersion method of Multi-Walled Carbon Nanotubes (MWCNTs) in aqueous medium

Carlos Rodríguez1, Ederley Vélez1, Julián Restrepo1, Jorge H. Quintero2, Rodrigo Acuña3
1 Facultad de Ciencias Básicas. Universidad de Medellín. Medellín, Colombia
2 Escuela de Física. Universidad Industrial de Santander, Bucaramanga, Colombia
3 Universidad Nacional de Colombia, Medellín, Colombia

*e-mail: crodriguez@udem.edu.co

Abstract. The carbon nanotubes (CNTs) dispersion has gained interest in recent years due to its multiple applications in fields such as electronics, concrete, optics, environmental, automotive, marine and aeronautics coatings. In this sense it is necessary to develop stable dispersions of CNTs. On a laboratory scale the method of preparation of the CNTs is usually done using sonication, but this method is not appropriate to obtain CNTs dispersions on a larger scale. This work studies Multiwalled Carbon Nanotubes (MWCNTs) in aqueous medium comparing an industrial laboratory dispersion method vs traditional sonication. A factorial experimental design was performed, considering as variables: dispersion method, type of surfactant and use of a rheological modifier. The samples were prepared according to the full factorial DoE and properties such as electrical conductivity and pH were studied. Stability measurements were carried out over time and charge stability studies were performed using zeta potential measurements. The results shown the best combination of variables for the electrical conductivity was: dispersion method, sonication; dispersant, TX-100; rheological modifier, present. Although the results show that an improvement in CNTs dispersion is not achieved with the grinding and the use of industrial additives, the additive Disperbyk 2012 presented the highest value of electrical conductivity as a lonely compound, but the final electrical conductivity obtained when using it was not so high, it indicates that this additive must have specific conditions of activation, which implies that a further experimental work is required in order to get a suitable working window that allows a combination of variables with greater industrial application.

1. Introduction

Carbon nanotubes (CNTs) are cylindrical structures obtained from carbon of nanometric diameter, strong and flexible [1]. Specifically, CNTs can be classified as single-walled carbon nanotubes (SWCNTs) or multiple-walled carbon nanotubes (MWCNTs). Several researchers have identified the emerging importance of the use of CNTs as advanced materials to improve performance in the physical, chemical and mechanical properties of various materials (plastics, polymers, concrete, paints, coatings, adhesives, among others), due to their high electrical conductivity and its superior thermal and mechanical properties, compared with other materials [2] [3-5]. Some works reported the use of carbon nanofibers (CNFs) and carbon nanotubes (CNTs) to enhance the mechanical properties of composites based on their particular properties and exceptionally high aspect ratios, so nanocarbons (NCs) have shown to be beneficial nanomaterials for nano-reinforcement [6]. They also function as electrically conductive fillers in plastics, to dissipate static charges in electrical and electronic equipment, and in car body panels that can be painted electrostatically [7]. Through the use of CNTs, polymers can be modified to make them more resistant to temperature, aggressive chemicals, corrosive environments, extreme pressures and abrasion [8]. Even its use in matrices of conglomerating materials is reported as a route to develop Portland cement matrices with a variety of mechanical and electrical properties [9]. This is how CNTs are, therefore, considered to be the most interesting nanomaterials with greater application potentials [10]. The NCs dispersion is one of the key factors that strongly influence the properties of nanocomposites. Several researches have been carried out with chemical agents to achieve a consistent dispersal of carbon nanomaterials in water, although, if the process is uncontrolled, it can shorten or damage the NCs or even dissolve them, and this can have a negative effect on the composites as well. Therefore, if NCs are to be used as reinforcement for composites, physical methods have to be
employed to disperse the NCs before they can be mixed into the composites [6]. In this sense, it has been found that the main limitation for its use is to have them completely dispersed in a suitable vehicle (water, an organic solvent, oil or polymer), since it is required that said dispersion remain stable during the storage time, in when its viscosity characteristics and not sedimentation of CNTs, while retaining its other attributes, without losing physical or mechanical properties [11]. It should be noted that the use of sonication is an effective method for obtaining dispersed carbon nanotubes [12]. One of the most practical ways to use them in different applications is to have them in a dispersion state, which facilitates their use and handling, since they are very difficult to disperse, due to their high surface area and potential to agglomerate.

This work studies dispersions preparation of Multiwalled Carbon Nanotubes (MWCNTs) at 0.35% solids in aqueous medium as a study on an industrial scale and to improve its stability during storage. A factorial experimental design was performed, considering as variables: dispersion method, type of surfactant and rheological modifier. The samples were prepared according to the full factorial Design of Experiments (DoE) and properties such as electrical conductivity and pH were studied.

2. Experimental Setup

2.1 Materials
Multi walled carbon nanotubes (MWCNT) produced by Nanocyl; Triton X-100 (TX-100, pH = 4.07, K = 63.4 μS/cm) of 98% purity produced by Sigma Aldrich; Disperbyk 2012 (non-volatile matter = 40%, pH = 4.75, K = 535.0 μS/cm, carrier = water) produced by BYK-Chemie; Invecryl 601A (non-volatile matter = 40%, pH = 6.75, K = 31.6 μS/cm) produced by Invesa S.A (a local producer); BYK-7420 (non-volatile matter = 40%, pH = 6.12, K = 17.8 μS/cm, solvent = amide ester) produced by BYK-Chemie; deionized water (pH = 6.19, K = 2.9 μS/cm). The reagents were used as received.

2.2 Experimental Design (DoE)
The dispersions preparation of multiple wall carbon nanotubes (MWCNTs) at 0.35% solids in aqueous medium (deionized water) was studied using full factorial experimental design of 12 trials ($2^3 \times 1$), considering as variables: a) Dispersion method: ultrasonic and bead milling. The objective is to compare the efficiency of both dispersion techniques, considering the use of ultrasonic tip is not yet employable on an industrial scale and there is not available a large usable equipment; b) type of surfactant: ethoxylated octylphenol (TX-100, amphoteric surfactant), controlled polymerization copolymer (Disperbyk 2012) and uncontrolled polymerization copolymer (Invecryl 601A). The objective is to compare the efficiency of a conventional surfactant such as the TX-100 with surfactants for industrial use, which have performance and environmental advantages; c) rheological modifier: A rheological additive (modified urea) as absent and present was used. Due to its low viscosity and solids content, the dispersion of MWCNTs may require the use of a rheological agent (see Table 1).

2.3 MWCNTs dispersion using ultrasonic tip.
Aqueous dispersions were prepared using the three types of dispersing agents: TX-100 (amphoteric surfactant), Disperbyk 2012 (controlled polymerization copolymer) and Invecryl 601A (non-polymerized polymerization copolymer). Dispersions were sonicated using an ultrasonic tip, which applied a total energy of 390 J/g to guarantee an adequate dispersion degree. Sonication was carried out in a 500 W ultrasonic processor set to 40 % amplitude in 20 seconds on/off.

2.4 MWCNTs dispersion using milling media.
Aqueous dispersions were prepared using the three types of dispersing agents: TX-100 (amphoteric surfactant), Disperbyk 2012 (controlled polymerization copolymer) and Invecryl 601A (non-polymerized polymerization copolymer). Dispersions were prepared using a high-speed laboratory disperser batch-wise operated vertical stirred media mill. The milling media consists of spherical zirconia beads of 2.0 mm (ZrO$_2$·SiO$_2$, density = 3.7 g/mL), using a 75% capacity of the milling chamber.
The stainless-steel milling chamber of 2000 mL of capacity had 2 Teflon dispersing discs (50mm/60mm). The chamber had a double-shell enables the jacket cooling for the temperature control of the mill charge. The dispersion process was operated at 2,800 rpm by 8 hours.

2.5 Characterization.
The MWCNTs dispersions prepared were characterized by pH and electrical conductivity measurements using a Cole-Parmer PC100 pH/Conductivity Meter with electrode ref. WZ-59200-06, combined glass electrode (Ag/AgCl). Prior measurements the samples were subjected to agitation in an ultrasonic bath by 10 minutes. The zeta potential measurements were obtained using a Zetasizer Nano ZS (Malvern) equipped with a Laser source of wavelength of 633 nm and operating at a scattered angle at 173° and with Zetasizer Software version 7.11. using disposable cells (DTS 1070). It is important to mention that it was not possible to obtain UV-vis measurements because the combination of additives used presented interference with the absorption band of the nanotubes at 260 nm.

3. Results and discussion
The pH and electrical conductivity were studied as response variables, considering the main application for the MWCNTs to improve the electrical conductivity in concrete and other materials. The samples in Table 1 were prepared and after 24 hours, the pH and electrical conductivity measurements were made (see Table 1). These results were analyzed according the DoE variables and results reported according to the study variables (see Table 2).

| test # | variable 1 | variable 2 | variable 3 | pH   | conductivity (μS/cm) | Temp (°C) |
|--------|------------|------------|------------|------|----------------------|-----------|
| 1      | sonication | TX-100     | absent     | 6.58 | 2103.3               | 26.2      |
| 2      | sonication | TX-100     | BYK D-420  | 5.44 | 6660.0               | 26.8      |
| 3      | sonication | Disperbyk-2012 | absent | 5.52 | 1265.7               | 26.2      |
| 4      | sonication | Disperbyk-2012 | BYK D-420 | 5.32 | 1128.3               | 26.3      |
| 5      | milling    | TX-100     | absent     | 8.63 | 733.3                | 28.9      |
| 6      | milling    | TX-100     | BYK D-420  | 7.24 | 725.0                | 26.8      |
| 7      | milling    | Disperbyk-2012 | absent | 7.64 | 290.3                | 28.4      |
| 8      | milling    | Disperbyk-2012 | BYK D-420 | 6.60 | 633.0                | 27.4      |
| 9      | sonication | Invecryl 601A | absent | 8.55 | 4560.0               | 28.3      |
| 10     | sonication | Invecryl 601A | BYK D-420 | 7.10 | 3958.7               | 28.5      |
| 11     | milling    | Invecryl 601A | absent | 8.95 | 533.0                | 28.4      |
| 12     | milling    | Invecryl 601A | BYK D-420 | 7.97 | 998.7                | 27.8      |

Table 2: Results obtained according to DoE analysis

| variable        | level    | pH   | electrical conductivity |
|-----------------|----------|------|------------------------|
| dispersion method| sonication | 6.16 | 2708.0                |
|                 | milling   | 7.39 | 513.7                 |
| dispersing agent| TX-100    | 6.61 | 2216.5                |
|                 | Disperbyk-2012 | 5.99 | 756.3                |
|                 | Invecryl 601A | 7.72 | 1859.8               |
| rheology modifier| absent   | 7.41 | 1227.3                |
|                 | present   | 6.14 | 1994.3                |
According to Table 2, the better variables combination (criterion of greater is better for electrical conductivity): Dispersion method, sonication; dispersing agent, TX-100; rheological modifier, present. Only electrical conductivity was considered, because no direct relationship was found between the pH and the final electrical conductivity. When analyzing the interaction between the variables: A strong interaction is observed between the type of dispersant and the dispersion method (as well as the rheological modifier). It is verified that the performance of the dispersing additive depends on the dispersion method and the associated conditions and a very slight interaction between the scattering method and the rheological modifier is observed which indicates that both variables are practically independent. There is no simple relationship between pH and electrical conductivity for all data. However, it is appreciated that a relationship can be obtained, depending on the variable analyzed so the pH was analyzed vs. the electrical conductivity by group of variables: When sonication is employed, there is a relationship between pH and electrical conductivity, if the rheological modifier is absent. On the other hand, when milling is used, there is a relationship between pH and electrical conductivity, if the rheological modifier is present. That is, both dispersion methods have an interaction with the rheological modifier but this is different. When analyzing the data for each dispersant as a function of pH vs electrical conductivity (for the TX-100 and the Disperbyk 2012), when the pH increases, the electrical conductivity decreases. In the case of the Invecryl 601A, no relationship between both variables was observed. This indicate there is a similar stabilization method between TX-100 and Disperbyk 2012, but different from the effect of the Invecryl 601A. Stability studies were carried out in time: Measurements on the dispersions stored 1, 30, 60 days and the pH and electrical conductivity properties were measured (see Figure 1). From Figure 1, for both properties it is observed that after 30 days there is an increase in both properties in a similar way. But at 60 days, the properties are again comparable to those obtained after 1 day of preparation.

Zeta Potential measurements were performed for samples with the highest electrical conductivity (both dispersion methods) (see Figure 2): Using sonication a Zeta Potential of -20.8mV was obtained and for milling of 16.2 (with two peaks at 8.90mV and 38.5mV).

Figure 1. Variation of properties for 1, 30 and 60 days: a) pH variation on time; b) electrical conductivity variation on time

Figure 2. Zeta Potential stability studies: a) Zeta potential for test # 2 obtained by sonication; b) Zeta potential for test # 12 obtained by milling.
4. Conclusions

Both of the dispersion methods tested leads to CNTs dispersions with incipient stability (range from ±10 to ±30 mV), but the milling dispersion (industrial method) leads to an interesting result: Two peaks are obtained, one of them with incipient instability in the Zeta Potential (range from ±10 to ±30 mV), but the other peak (38.5 mV) indicates there is moderate stability of particles (range from ±30 to ±40 mV), which indicates the industrial method tested could provide stable dispersions, even though this method requires a longer dispersion time, improve the dosage, type of dispersant used or combination of these. The sonication dispersion (traditional method) shows to be 5 times more efficient than milling, which indicates that this dispersion technique is appropriate to achieve the CNTs dispersion. Some innovative alternatives to milling dispersion (conventional method) can be considered with the so-called “nano-milling dispersion”, which would be ideal for this application, but the equipment required is very expensive and scarce even on an industrial laboratory scale.

The fact additive Disperbyk 2012 presented the highest value of electrical conductivity as a lonely compound, but the final electrical conductivity obtained when using it was not so high, it indicates that this additive must have specific conditions of activation, which implies that a further experimental work is required in order to get a suitable “working window” that allows a combination of variables with greater industrial application. The dispersing additive TX-100 has shown the best efficiency in combination with sonication dispersion, but considering the environmental restrictions related to this type of surfactants, it is ideal to look for a cost-effective alternative for this. However, the TX-100 and ultrasound combination shows to be the most efficient combination of variables.

Acknowledgements

This work was supported by Project 985 of Vicerrectoría de Investigaciones of Universidad de Medellín. Special thanks to Universidad Nacional de Colombia (facilitated the use of the tip sonicator) and the authors also gratefully acknowledge to Centro de Laboratorios of Universidad de Medellín.

References

[1] Drexler, K.E., 1992 Nanosystems: Molecular Machinery, Manufacturing and Computation. New York: John Wiley & Sons.
[2] Wang, X.; Li, Q.; Xie, J.; Jin, Z.; Wang, J.; Li, Y.; Jiang, K.; Fan, S., 2009 Nano Letters. 9 (9) 3137.
[3] Mendoza Reales, O.A.; Arias Jaramillo, Y.P.; Ochoa Botero, J.C.; Delgado, C.A.; Quintero, J.H.; Toledo Filho, R.D. 2018 Cement and Concrete Research 107 101-109.
[4] Mendoza Reales, O.A.; Ocampo, C.; Arias Jaramillo, Y.P.; Ochoa Botero, J.C.; Quintero, J.H.; Silva, E.C.C.M.; Toledo Filho, R.D. 2018 Hindawi Advances in Civil Engineering 2057940.
[5] Rodriguez, B.; Quintero, J.H.; Arias, Y.P.; Mendoza-Reales, O.A.; Ochoa-Botero; J.C.; Toledo-Filho, R.D. 2017 IOP Conf. Series: Journal of Physics: Conf. Series 935 012014.
[6] Alsharefa, J.; Tahaa, M.; Khana, T., 2017 Journal Teknologi, 79 (5) 69-81.
[7] a) Mittal, G.; Dhond, V.; Rhee, K.Y.; Park, S-J.; Lee, W.R. 2015 J. Ind. Eng. Chem. 21 11-25; b) Bachtold, A. Hadley, P.; Nakani shi, T.; Dekker, C., 2001 Science 294(5545) 1317-1320; c) Schadler, L.S.; Giannaris, S.C.; Ajayan, P.M., 1999 Appl. Phys. Lett. 73 3842-3844.
[8] Coleman, J.N.; Khan, U.; Blau, W.J.; Gunko, Y. K. 2006 Carbon 44 (9) 1624-1652.
[9] Li, G.Y.; Wang, P.M.; Zhao, X., 2005 Carbon 43 (6) 1239-1245.
[10] Huhtala, M.; Kuronen, A.; Kaski, K. 2002 Computer Physics Communications 146 (1) 30-37.
[11] Jiang, L.; Gao, L.; Sun, J. 2003 Jour. Coll. Interf. Sci. 260 (1) 89-94.
[12] Yu, J.; Grossiord, N.; Koning, C.E.; Loos, J., 2007 Carbon 45 (3) 618-623.