

Setting in suspension of double-walled carbon by some biopolymers: characterization by Turbiscan

Karima Seffah^{a, b*}

^a Université Benyoucef Benkhedda Alger 1, Algérie

^b Equipe Mécanique des Matériaux Fibreux, Unité de Recherche (UR-MPE), Université M'hamed Bougara, Algérie

*Corresponding author, email: karimafella@yahoo.fr

Selected paper of JSSE'18, received in final form: March 4, 2019 ; accepted date: March 23, 2019

Abstract

Our present study consists of the formulation and characterization of suspensions of double-walled carbon nanotubes (CNTs) using two biopolymers of natural origin (lecithin and proteins). Soy lecithin and sodium caseinate are two biodegradable and non-toxic biopolymers, they are widely used as an ingredient in the food industry.

The operating conditions of dispersion such as the power and the duration of sonication as well as the dispersant/NTCs report/ratio, were optimized. Stability was demonstrated by the Turbiscan technique, and confirmed by zeta potential measurements over time. The Turbiscan has proven to be a non-invasive, efficient and convenient tool for analyzing the stability of CNTs suspensions.

Keywords: Double walled carbon nanotubes, biopolymère, stability, Turbiscan

1. Introduction

Carbon nanotubes, since their discovery in 1991 by Iijima[1], are of great interest to the scientific community because of their chemical nature, their structure, and the strong anisotropy of these particles, which gives them exceptional properties. These excellent properties make NTCs materials promising for many applications, such as hydrogen storage [2], catalyst supports [3], chemical sensors [4] and electronic devices [5]. These new nanomaterials are intrinsically hydrophobic, they agglomerate and sediment rapidly in water as well as in most organic solvents [6].

It is often necessary to have stable suspensions of CNTs to manipulate and study them, whether for their functionalization or for the preparation of homogeneous composites and to envisage applications in different fields. Achieving stable suspensions of carbon nanotubes in water is always a challenge. To solubilize or disperse them, it is usually essential to modify their surface properties. To improve their interactions with the solvent, two main approaches exist: the chemical functionalization of the surfaces of the CNTs and the physical adsorption of the amphiphilic molecules on their surface.

In this study, we will focus exclusively on adsorption dispersions of molecules on the surface of NTCs. This method is the most used because it has the advantage of being achieved in mild chemical conditions.

Thus, it makes it possible not to modify the atomic and electronic structure of carbon nanotubes and to avoid the alteration of their mechanical properties. The addition of surfactants is desirable because it leaves intact the intrinsic properties of the NTCs. However, for different applications, the potential toxicity of the surfactant is an important issue. Non-toxic amphiphilic biopolymers are a good alternative [7].

In this work we will focus exclusively on aqueous dispersions with two non-toxic natural biopolymers. Soy lecithin and sodium caseinates are biodegradable and non-toxic biopolymers. They are widely used as an ingredient in the food industry, are natural emulsifiers. Soy lecithin molecules and sodium caseinates have a lipophilic pole and a hydrophilic pole; they are therefore amphiphilic [8].

To evaluate the stability of the suspensions; There are some ways such as microscopy spectroscopy, turbidity analysis. However, these means are only applicable to diluted emulsions. Electron microscopy (SEM, TEM) is commonly used to verify the good dispersibility of NTCs. Nevertheless, it is an expensive and difficult technique to set up routinely. The Turbiscan method is an alternative, which can be used for real-time monitoring of concentrated and opaque emulsions. Turbiscan technology consists of measuring transmitted and backscattered light every 40µm on the height of the sample, in order to detect and quantify size variations (coalescence, flocculation) and phase separations (sedimentation, creaming). Turbiscan makes it possible to

identify and quantify the stability of NTCs dispersions in a few hours. The measurements are made under actual solvent conditions without dilution. In this perspective, our present study consists in the formulation and characterization of suspensions of double-walled carbon nanotubes using polymers of natural origin.

2. Experimental section

The double-walled carbon nanotubes were synthesized at the CIRIMAT of Toulouse (France) by the chemical vapor deposition method [9]. Soya lecithin was supplied by Lipoid (France). The sodium caseinate used for this study, supplied by Armor Proteines (France) and produced by precipitation, has a protein purity of 92.7% m / m (supplier data).

2.1. Dispersion procedure of double-walled carbon nanotubes in water

In order to prepare homogeneous dispersions; an ultrasonic probe (Model Vibra cell 75042, 20 kHz, 500 W) was used. The apparatus at summer was used at 30% amplitude, during 30 min with apulse of 5s on, 5s off. Suspensions containing CNTs were prepared using different biopolymers. Several bio biopolymers concentrations were studied 50, 500 and 1000 mg/L. Suspensions containing 50 mg / L of CNTs were prepared using the bio-polymer as a surfactant. Stable suspensions were obtained at a concentration of 50 mg/l for sodium caseinate and 500 mg / l for soy lecithin.

2.2. Turbiscan measurements

Turbiscan, based on multiple light scattering, is an optical analyzer. It can be used to monitor reversible (creaming and sedimentation) and irreversible (coalescence and flocculation) destabilization phenomena in a concentrated and opaque emulsion without dilution. It can detect phase changes much earlier and easier than classic approaches. The formulation stability was monitored using a Turbiscan MA 1000 (LGC, Toulouse, France). The apparatus has a detection head equipped with a near-infra-red light source (860 nm) which scanned the sample length vertically by mean of a step-by-step motor. Ten milliliters of suspensions sample was placed in a flat-bottomed screw-cap cylindrical glass tube, tightly sealed. The tube was then scanned (48 sweeping of 30 minute during 24 hours).

2.3. Zeta potential measurements

Zeta potential (ξ) measurements were carried out with zetasizer (Model ZEN 3691, Malvern Instruments).

Our measurements were performed with between 3 and 5 mL of suspensions. These suspensions were redispersed (by bath sonication) just before the injection into the setup. All the measurements were performed in optically clear suspensions, The suspension has to be neither too concentrated (the Laser would not cross the sample) nor too diluted (absence of signal). The reported results are the average of at least three full repeat experiments .The repeated tests showed a measurement error of ± 2 mV.

3. Results

Transmission and backscatter profiles recorded using Turbiscan MA1000 represent the state of a suspension in a sedimentation column. They make it possible to detect very early if the suspension sediments or agglomerates or if the two phenomena occur simultaneously.

The phenomena relating to the stability of dispersed media can be detected qualitatively by observation of backscatter profiles. Stable suspensions are characterized by constant backscatter levels over time throughout the column, that is to say that successive sweeps of the sample give profiles which are superimposed on the initial profile (profiles at $t = 0$). If, on the contrary, the backscattering level decreases (or increases) after a certain number of sweeps compared to the initial sweep, the suspension is the seat of agglomeration phenomena [10].

For the analysis of our samples, 10 ml of suspensions were placed in the measuring cell and in automatic sweeping mode (48 sweeping for 30 minutes for 24 hours).The Turbiscan MA1000 sweeps the sample for several hours and thus analyzes the evolution of the transmission over the height of the tube. The Y axis represents the flux intensity and the X axis represents the postions in the tube (Figure.1).

The measurements show that over this analysis period, the transmission levels are uniform and invariant over time over the entire length of the sample. These results indicate that the suspensions are stable and also indicate the absence of sedimentation. The transmission profile indicates the absence of variation in particle size. It can be concluded that the suspensions are stable and homogeneous. Its results confirmed by zeta potential measurements (Figure. 2).

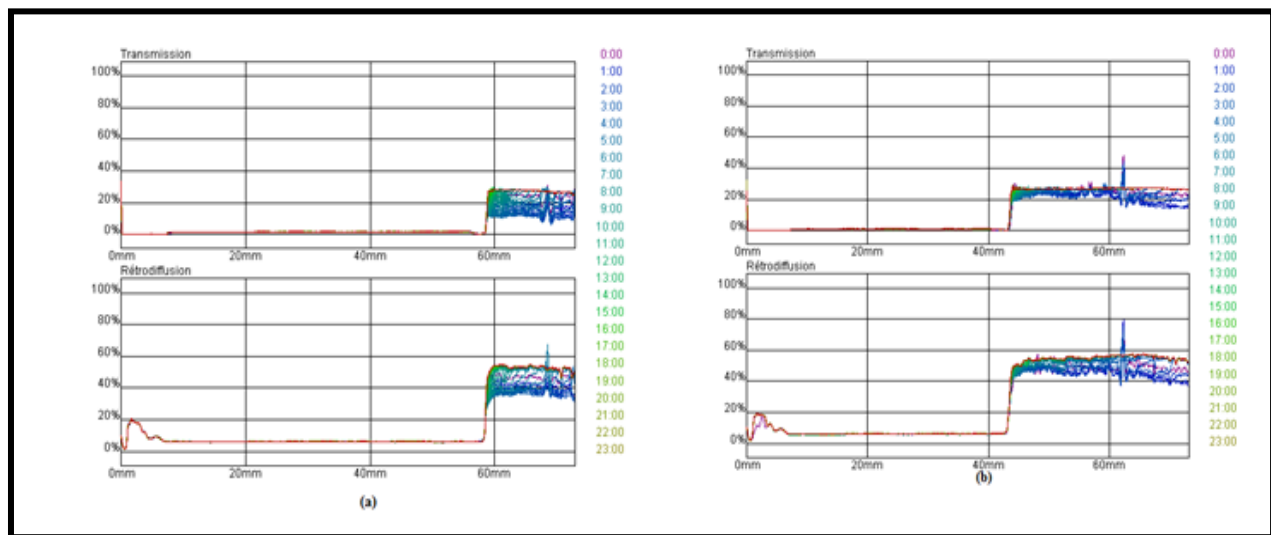


Figure1: (a) Transmission profiles (top) and backscatter (bottom) depending on the height of the tube as a function of time for the suspension of soy lecithin 500g / l. (b) Transmission profiles (top) and backscatter (bottom) depending on the height of the tube as a function of time for the suspension of sodium caseinate 50 g / l

In general, suspensions with a zeta potential above 30 mV (absolute value) are physically stable, suspensions with a potential above 60 mV show excellent stability. Suspensions below 20 mV are of limited stability; below 5mV the suspensions undergo a pronounced aggregation [11]. The zeta potential (in absolute value) of the NTCs sodium caseinate suspension over time varies between 22 Mv and 28Mv (Figure 3 (a)); and for suspension NTCs soy lecithin varies between 38Mv and 44 Mv (Figure 3 (b)).

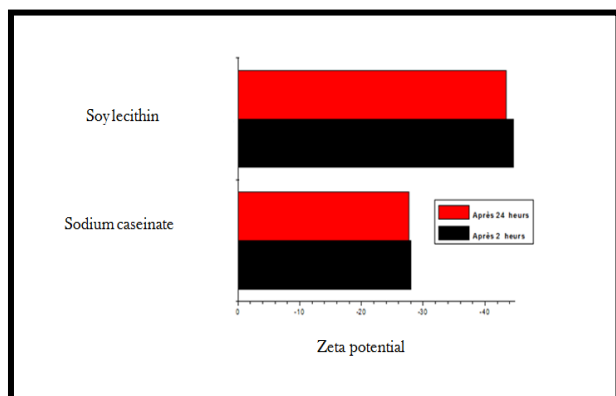


Figure.2: Zeta potential measurements on suspensions dispersed by both biopolymers.

The suspensions have good stability over time. These results can be attributed to the strong adsorption capacities of the hydrophobic tails of soy lecithin and sodium caseinate on the surface of bi-walled carbon nanotubes.

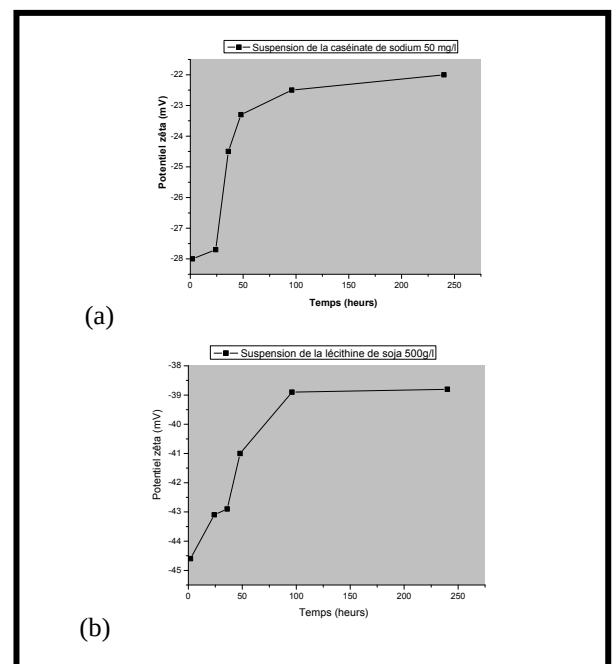


Figure.3:

(a) Measurement of the zeta potential of the NTCs suspension Sodium caseinate.

(b) Measurement of the zeta potential of the NTCs soy lecithin suspension.

4. Conclusion

The objective of this study is the suspension of double-walled carbon nanotubes by two biopolymers. And in a second time carried out the characterization of the NTCs suspensions by the Turbiscan technique.

The operating conditions of dispersion such as the power and the duration of sonication as well as the ratio dispersant / CNTs, were optimized.

Stability has been demonstrated by the Turbiscan technique; and confirmed by zeta potential measurements over time. Turbiscan has proven to be a non-invasive, efficient and convenient tool for analyzing the stability of CNTs suspensions.

Acknowledgments

The authors gratefully acknowledge the Ministry of High Education and Scientific Research (Algeria) and the French Ministry of Foreign and European Affairs for financial support of PHC- TASSILI 10MDU797 project.

Reference

- [1] S. Iijima 1991, *Nature*. 354 (1991)56-58.
- [2] S.M. Lee, Y.H. Lee, *Applied Physics Letters*. 76(2000)2877-2879.

- [3] G.L. Che, B.B. Lakshmi, E.R. Fisher, C.R. Martin. *Nature* 393(1998)346-349.
- [4] P.G. Collins, K. Bradley, M. Ishigami, A.Zettl. *Science* 287(2000)1801-1804.
- [5] P.G. Collins, A. Zettl, H. Bando, A. Theses, R.E. Smalley. *Science* 278(1997)100-102.
- [6] H. Yu , S. Hermann , S. E. Schulz , T. Gessner , *Chemical Physics* (2012).
- [7] C.Tang, T. Zhou, J. Yang, Q. Zhang. *Colloids and Surfaces B: Biointerfaces* 86 (2011)189-197.
- [8] J.Morelle.Edition VARIA, Paris (1965) 283-298.
- [9] E. Flahaut, R. Bacsá, (a) A. Peigney,C.Laurent. *Chemical Commun* 12, (2003)1442-3.
- [10] C. R. Villatte, Doctorate thesis, 2010, University of Rennes
- [11] P. Lukanov, Doctorate thesis, 2010, University of Paul Sabatier(France)