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# Chemical functionalization of Xanthan gum for the dispersion of double-walled carbon nanotubes in water

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## A B S T R A C T

Achieving stable suspensions of carbon nanotubes (CNTs) in water is still a challenge. Addition of surfactants is desirable as it allows keeping intact the intrinsic properties of the CNTs. However, for different applications, the potential toxicity of the surfactant is an important issue. Polysaccharides are among the best candidates and chemical modification can improve their intrinsic features. They can thus combine the properties of added synthetic counterparts with their intrinsic biocompatibility. In this work, we focused on the synthesis of hydrophobically modified Xanthan (Xan) with three derivatives (Diphenylmaleic anhydride, Phthalic anhydride, Epichlorhydrin-Phenol) to disperse CNTs. The dispersion and the stability against sedimentation of double walled carbon nanotubes (DWCNTs) have been investigated (rheological properties, zeta potential) as a function of pH and Xan concentration. Our results show that stable suspension of DWCNTs for 0.5% (w/w) could be obtained with the three derivatives of modified Xanthan gum in acidic and alkaline media while Xan itself is a very poor dispersing agent for CNTs, giving good evidence of the validity of our approach.

## 1. Introduction

Due to their exceptional physical and chemical properties, such as excellent mechanical strength, high electrical and thermal conductivities, high specific surface area, low density, and high aspect ratio [1,2], CNTs have attracted considerable attention of researchers in various fields of research. Nevertheless, their insolubility in organic or aqueous media is a major bottleneck in the exploitation of these excellent properties because CNTs tend to agglomerate into bundles due to strong Van der Waals attractions forces. The poor solubility of CNTs turns dispersion into a challenge and several studies have already been published to achieve a uniform dispersion

in aqueous or organic media. Both covalent [3–6] and non-covalent [7,8] functionalizations of CNTs have been reported. However, a major drawback of covalent functionalization such as oxidizing treatment by the use of appropriate acids at high temperature (nitric acid alone, or in combination with sulfuric acid) is the disruption of the extended  $\pi$ -conjugation in CNTs, resulting into structural defects on the nanotubes and leading to decreased (or at least modified) electrical and mechanical properties [9,10]. In contrast, the non-covalent approaches usually involve ultrasonication, centrifugation and filtration, focus on spurring non-disruptive interactions such as  $\pi$ - $\pi$  stacking, adsorption, or Coulomb interactions through insertion of a chemical bridging agent [11], with

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surfactants, carbohydrates, proteins, and nucleic acids [12,13]. Thus, these approaches achieved by physical adsorption are usually relatively weak, keeping the structure of the native tubes. Therefore, the delocalized  $\pi$ -electron network of the CNTs sidewall is preserved ensuring a minimal perturbation of their properties [14].

Most available experimental methods to disperse CNTs in common solvents or polymers require using surfactants [15,16]. Recent reports suggest the use of ionic surfactants with high HLB (Hydrophilic-Liphophilic Balance) for dispersion and stabilization of CNTs in water. There is no preferred ionic one when organic solvents have to be used [14]. As a starting point in understanding CNTs dispersion in water and organic media, several parameters must be known, such as the nature of the surfactant, its concentration and type of interactions in the stabilized phase [17]. Previous works show no clear conclusion on the dispersive efficiency of either anionic or cationic surfactants [17,18]. Therefore, knowing the surface charge of CNTs is absolutely required to understand the adsorption mechanism with ionic surfactants and to predict colloidal stability of CNTs suspensions. Zeta potential analysis seems a useful tool to achieve this task. Thus, Jiang et al. [19] have shown that the surface of multi-walled carbon nanotubes (MWCNTs) in aqueous media is negatively charged. However, to shed some understanding on the behavior of single-walled carbon nanotubes (SWCNTs), Ausman et al. [20] have shown that highly polar solvents such as dimethylformamide (DMF), methylpyrrolidine (MP) and hexamethylphosphoramide (HMPA) are rather efficient to properly wet SWCNTs. Islam et al. [21] have obtained a stable dispersion in aqueous media of SWCNTs using dodecyl(trimethyl)azanium bromide. Anionic surfactants such as sodium dodecyl sulfate (SDS) [19,22–29] and dodecyl-benzene sodium sulfonate (NaDDBS) [30–32] have been widely used due to charge repulsion to limit the agglomeration tendency of CNTs [17]. Therefore, the former approach and the main driving force for surfactant-stabilized CNTs dispersions, the  $\pi$ - $\pi$  stacking interaction [33–35] between the benzene ring and the CNTs surface, is believed to significantly increase the binding of surfactant molecules onto CNTs [36]. Thus, by this approach, various aromatic molecules have been used, such as polycyclic aromatic compounds carrying pyrene moieties [37–40]. Furthermore, dispersed CNTs show great potential in the biomedical area, but the use of such aromatic surfactants in drug delivery applications is not recommended as they are toxic by inducing, for example, denaturation of proteins present in the blood [41]. Hence, as an alternative to potentially lowering this effect, biopolymers such as gum arabic or gelatin have been used to promote a good dispersion of CNTs in this field of application [42,43]. Iamsamai et al. [44] have used modified chitosan for the non-covalent surface modification of MWCNTs in aqueous media for drug delivery applications. Also, cellulose as an inexpensive, nontoxic, environmentally friendly and mass produced renewable material, has been used to form stable complexes with SWCNTs for pH varying between 6 and 10 [45]. Whether for sensing or for any other intended application, bridging CNTs with biological systems should be essential in designing life sciences-related tools employing these nanomaterials. More recently in this context, as an alternative method for produc-

ing MWCNTs dispersions, one type of non-covalent functionalization has received considerable attention involving biocompatible polymers (gum arabic and carboxymethylcellulose) to investigate their ecotoxicity on the amphibian larvae [46]. Also, Roman et al. [47] have demonstrated that amino acids can adsorb through non-covalent interactions with CNTs through favorable adsorption pathways. Biopolymers, such as polysaccharides with a good toxicological profile, bring both steric repulsion and better stabilization (as thickeners) of the aqueous phase behavior of these colloids. Besides being renewable, the unique structure of polysaccharides offers many interesting properties like hydrophilicity, biocompatibility, biodegradability (at least in the original state), stereoregularity, multichirality, and polyfunctionality, i.e. reactive functional groups (mainly OH-, NH-, and COOH-moieties) that can be modified by various chemical reactions [48]. Therefore, in the general context to achieve the stabilization of double-walled carbon nanotubes (DWCNTs) dispersion in aqueous media, we focused on the synthesis of hydrophobically modified polysaccharide. We first propose the hypothesis that the benzene ring can interact strongly with CNTs yielding a homogeneous dispersion. Thus, among water-soluble biopolymers, Xanthan gum (Xan), a microbial biopolymer produced by the *Xanthomonas campestris* with a high molecular weight (Fig. 1) [49,50] seems a promising candidate.

The main goal of this paper is thus to synthesize new Xan derivatives, based on the grafting of hydrophobic moieties (benzene ring) along the polysaccharidic chain and to investigate how such derivatives of Xan should prevent the agglomeration of DWCNTs in water through steric stabilization via hydrophobic interactions, and thus result in improved dispersibility of suspensions. In the present letter, we report on the synthesis of three derivatives of Xan (Diphenylmaleic anhydride, Phtalic anhydride, Epichlorhydrin-Phenol) (XDPMA, XPA, XEPH) and we compare their efficiency to disperse and stabilise DWCNTs in water using Zeta potential and viscosity measurements of the supernatant of centrifuged dispersions versus pH. Other parameters such as the number of walls and the length of CNTs of course also play an important role in terms of stability of the suspensions, as they respectively increase the density of the CNTs or the chances of contacts between the nanotubes, and thus potentially lead to more

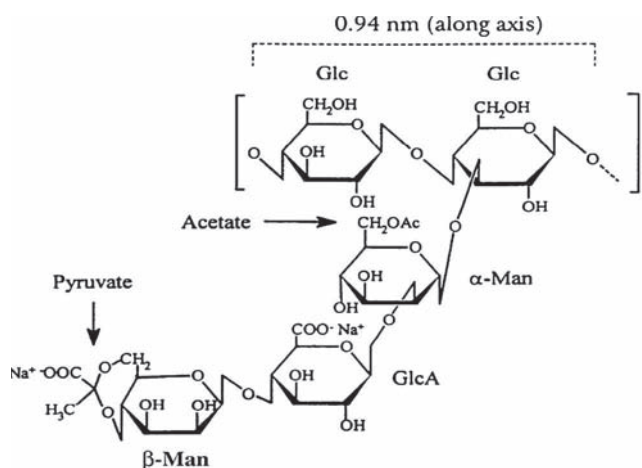


Fig. 1 – Chemical structure of Xanthan [49,50].

sedimentation and agglomeration. However, our approach is based here on the surface modification of the CNTs in order to enhance the interaction between the CNTs and the dispersing agent, and in this case, only the outer wall is concerned. With this hypothesis, the conclusions of this study should be very general and could be transposed to any kind of pristine carbon nanotube (excluding oxidized carbon nanotubes and other surface functionalization). The originality of this work is also to open a path for a family of new macromolecules to enhance the dispersion of CNTs in aqueous media, which could be very useful for the investigation of their toxicity in biological systems.

## 2. Experimental

### 2.1. Chemicals and DWCNTs synthesis

DWCNTs (ca. 80%) were synthesized by catalytic chemical vapour deposition (CCVD) with an outer diameter ranging between 1.2 and 3.2 nm; they are individual or gathered in small-diameter bundles (10–30 nm) which can be up to ca. 100  $\mu\text{m}$  in length [51]. Xanthan gum fine powder, cream colored (Rhodia, Standard 50-mesh), zinc-tetrafluoroborate hydrate crystallized salt; 2,3-diphenylmaleic anhydride (DPMA), phthalic anhydride (PA); N,N-dimethylformamide (DMF), acetone (ACT), ethanol (EA), epichlorhydrin and phenol were purchased from Sigma-Aldrich and were used as received.

### 2.2. Synthesis of XDPMA, XPA and XEPH

The most probable pathway of reactions of Xan derivatives, are either in heterogeneous (Fig. 2(a and b)) or homogeneous medium (Fig. 2(c)). Two working methods have been applied as described elsewhere by Hamcerencu et al. [52], Rogovin et al. [53] and Fournier et al. [54]. Moreover, leading to a step-wise increase in the hydrophobicity of Xan derivatives might be not as easy, mainly due to the insolubility of Xan in a suitable medium and the conformational structure at supermolecular level [52]. Thus, the synthesis strategy we proposed, based on the grafting of hydrophobic groups (benzene ring) along the polysaccharidic chain (hydroxyl groups), relies on

the use of excess reactants to enhance the reactions. Therefore, a possible approach is to use 11 mol of each reactant per mole of Xan (11 hydroxyl groups per Xan macromolecule (Fig. 1)). The main procedures reported for the synthesis conditions of Xan derivatives are summarized on Fig. 2.

### 2.3. Dispersion procedure of DWCNTs in water

DWCNTs suspensions in water were prepared as follows. First, three stock solutions of the required amount of the three derivatives of Xan (0.5%, w/w) were prepared in deionized water by dissolving the required amount under magnetic stirring for 48 h (25  $^{\circ}\text{C}$ ) to ensure the total hydration of the biopolymers. Second, appropriate masses of DWCNTs (initial amount of 0.02% (w/w)) were added to the vials (25 ml) with XPA, XDPMA and XEPH at 0.5% (w/w). To further evaluate the nanotubes' dispersion, the mixtures were then bath sonicated (Bioblock T570, 35 KHz, 160 W) for 30 min, after which the resulting mixtures were also ultrasonicated with an ultrasonic probe (Model Vibra cell 75042, 20 kHz, 500 W) for 15 min at 25% amplitude with a pulse of 5s on, 5s off to prepare homogeneous dispersions. Afterwards, each prepared suspension was centrifuged at 16,000 rpm for 30 min in order to separate the sediment from the supernatant. Finally, the as-prepared suspensions were left to stand for 10 h and the resulting supernatants were collected.

### 2.4. $^1\text{H}$ NMR Characterization

$^1\text{H}$  NMR spectrum of the derivatives of Xanthan was recorded on Bruker advance (400 MHz) instrument equipped with a 5 mm probe type TBO, using  $\text{D}_2\text{O}$  solutions having a biopolymer concentration around 3  $\text{g L}^{-1}$ . The Strategies of the experiments are explained in detail elsewhere [52,55,56].

The successful chemical modification of Xan by the aromatic moieties was confirmed by  $^1\text{H}$  NMR spectra (Fig. 3(b–d)) compared with the spectrum of Xan (Fig. 3a); the spectra show signals for characteristic peaks of aromatic moiety protons present at  $\delta$  between 7.0 and 8.6 ppm for the three derivatives of Xan (Fig. 3: (b) XDPMA, (c) XEPH (d) XPA). Moreover, the weakly developed peaks are likely to be due to the low efficiency of the reactions. Indeed, the polysaccharidic chain of Xan, presents a conformational transition in

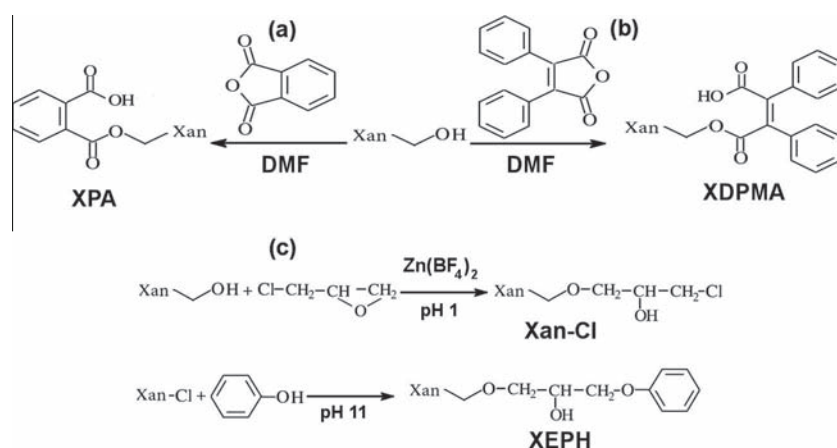


Fig. 2 – Procedures for the modification of Xanthan: (a) and (b) heterogeneous media [52]; (c) homogenous media [53,54].

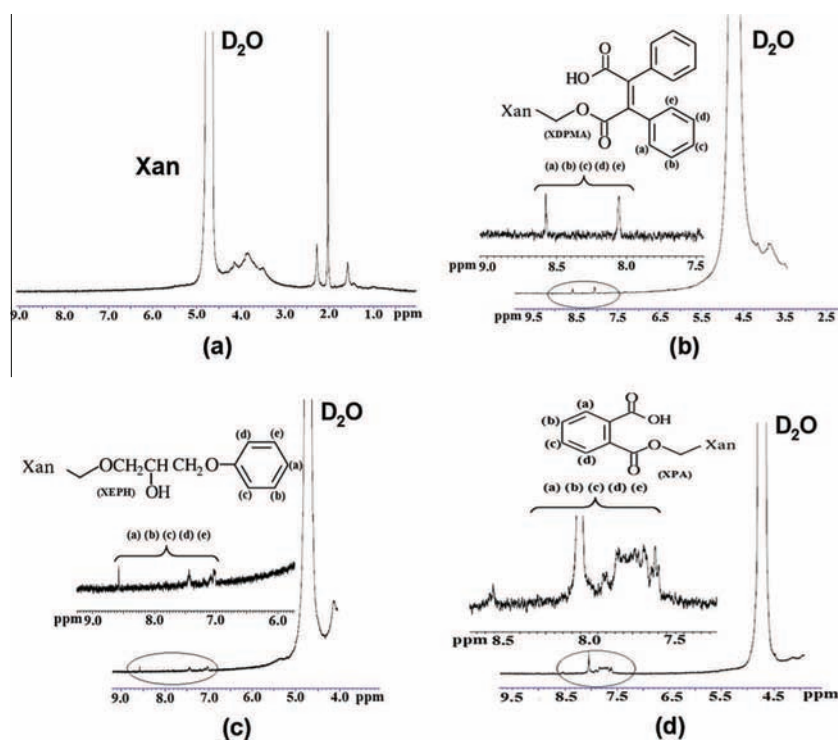


Fig. 3 – <sup>1</sup>H NMR spectra in D<sub>2</sub>O of Xan (a), XDPMA (b), XEPH (c) and XPA (d).

solution [57,58]. Therefore, the access of aromatic moieties to hydroxyl groups maybe to a rather low extent [52], yielding to a low degree of substitution.

### 2.5. Zeta potential measurements

Zeta potential ( $\xi$ ) measurements were carried out with zeta-sizer (Model ZEN 3691, Malvern Instruments). All the measurements were performed in optically clear suspensions, so it was necessary to make these measurements with samples having a much lower concentration of dispersing agent (Xan derivative) than these used in the rheological studies. The effective charge of colloidal particles is typically affected by some physicochemical parameters, among them the ionic strength and pH. Therefore, the  $\xi$ -potential of samples having 0.1% (w/w) of the three derivatives of Xan as a function of pH in both acidic and basic medium were determined by automatically adding the required amount of HCl and NaOH. It should be noted that the values were measured from pH around 1.5 to 10 in order to obtain a better approximation and auxiliary information on the size distribution of dispersed DWCNTs.

### 2.6. Viscosity measurements

The shear rate dependent viscosity measurements were staged with a controlled strain rheometer (Physica Anton Paar, Germany), operating in concentric cylinder geometry and connected to a water bath in order to ensure a constant temperature of 25 °C. At this temperature the system was left to equilibrate for 30 min. The apparent viscosity was determined by measuring the viscosity at each shear rate, and all

the experiments were done using samples from the resulting supernatants (Section 2.3) at neutral pH.

## 3. Results and discussion

Three derivatives of hydrophobically modified Xan, XPA, XPDMA and XEPH were used at 0.5% (w/w) to disperse DWCNTs in water. As shown on Fig. 4, the  $\xi$ -potential of the dilute suspensions of DWCNTs versus pH for the three derivatives was extremely pH dependent and decreased significantly (absolute value) for pH < 5, reaching values ranging from -30 to -40 mV for pH above 5. These results can be attributed to strong adsorption ability of the hydrophobic tails of the Xan derivatives (benzene moiety) on the surface of

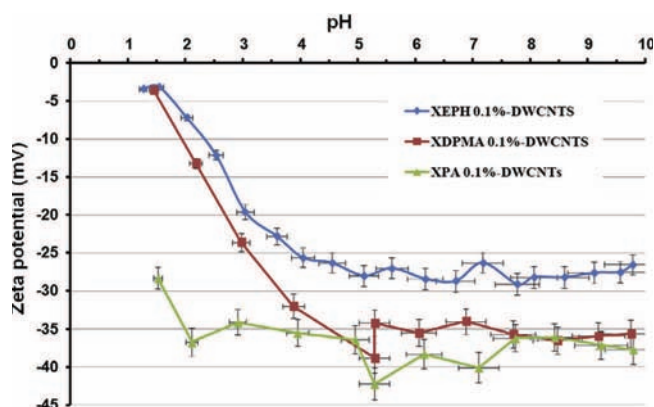
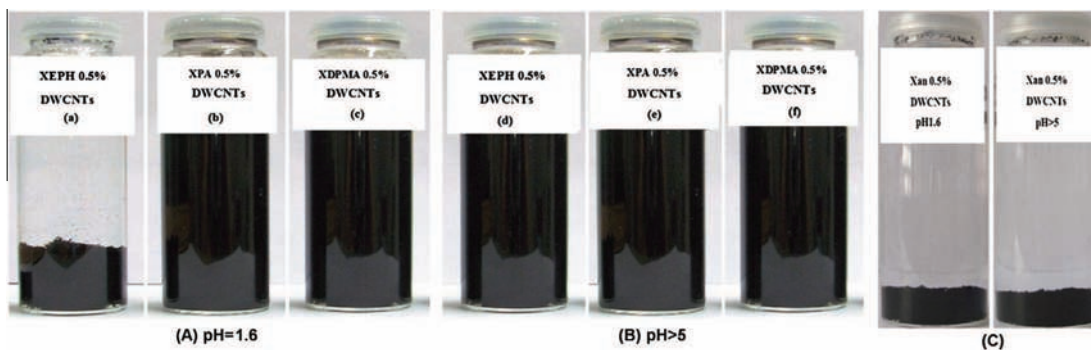


Fig. 4 – Plot of the  $\xi$ -potential as a function of pH of the dispersions samples.



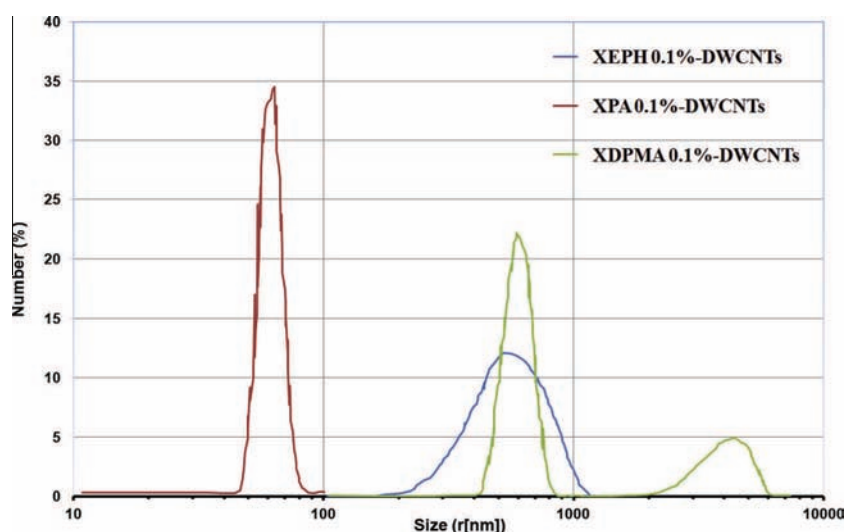


**Fig. 5 – Typical images of the dispersion efficiency of DWCNTs with XEPH; XPA; XDPMA; at 0.5%; (A): pH 1.6; (B): pH > 5, and (C) native Xan.**

DWCNTs. This is in agreement with Liu et al. [59], who reported that for CNTs dispersion in aqueous media, the relatively high value of  $\xi$ -potential make them stabilize due to Coulomb forces. Moreover, particles with zeta-potentials smaller than  $-15$  mV or larger than  $15$  mV are deemed to be stabilized by electrostatic repulsion interactions [60]. As shown in Fig. 4, for the XEPH/DWCNTs, it is clear that increasing pH from acidic to basic media, the  $\xi$ -potential reached  $\sim -30$  mV. The difference of the dispersion efficiency is shown on Fig 5A (a), the solution of XEPH (0.5%)/DWCNTs for pH around 1.6 appears more clear with DWCNTs agglomerated for  $\xi$ -potential near  $-5$  mV. Important information is obtained from this result, in particular the chemical structure of the aromatic moiety of the XEPH because this finding is in agreement with previous study by Clark et al. [11] who have demonstrated that the dispersion of CNTs in water is pH dependent due the chemical structure of the dispersing agent. Hydroxyl groups become ionized only under basic conditions while carboxylic acid groups are protonated at low pH. Hence carboxyl and hydroxyl groups bound to the aromatic moiety in the case of XPDMA and XPA which will allow for both protonated and ionized states to exist over the pH range from acidic to alkaline media, while hydroxyl groups presents in XEPH become ionized only under basic conditions. Thus, it

is important to point out that the enhanced dispersions observed are pH dependent. Therefore, extending the pH from acidic to alkaline conditions, more oxygenated groups become ionized resulting in a more negatively charged surface. In view of our results, the non-covalent functionalization of DWCNTs in aqueous media were found to have  $\xi$ -potential ranging from  $-30$  to  $-40$  mV which confirms the successful immobilization of Xan derivatives on DWCNTs by adsorption of the benzene moiety of the modified biopolymer on the surface of DWCNTs which have a superior ability of dispersing than native Xanthan (Fig. 5C), via  $\pi$ - $\pi$  stacking interactions between the benzene ring and the CNTs with pH values above 5 as shown on Fig. 5B. Fig. 6 illustrates the good agreements between the size distribution particles by numbers, and the surface charge density of colloidal particles dispersed by the three derivatives of Xan, leading to complex colloids with DWCNTs in aqueous media (pH  $\sim 7$ ), with size distributions by number ranging from 10 to 1000 nm.

Results suggest that a higher surface charge density provides a better stability of the suspensions. However, plotting the viscosity as a function of shear rate revealed that the presence of the benzene ring in the back bone of the modified xanthan increased the hydrophobic interactions, therefore, leading to a drop of the viscosity of the solutions at low shear



**Fig. 6 – Plot of the size distribution by number of the dispersion samples of DWCNTs pH  $\sim 7$ ; T = 25 °C.**

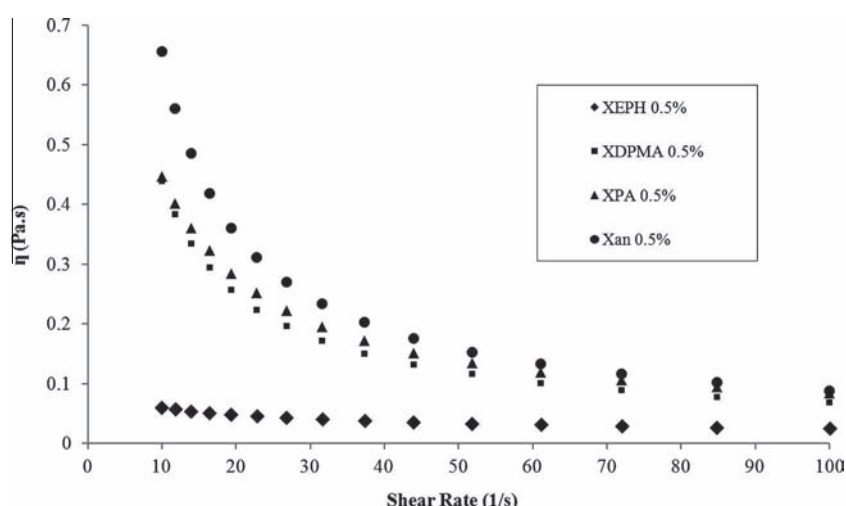


Fig. 7 – Plots of viscosity versus shear rate at 0.5% of Xan; XPA; XPDMA; XEPH at 25 °C, pH 7.

rate, as shown on Fig. 7. Consequently, the observed changes in viscosity of the native Xan and their derivatives (more pronounced in the case of XEPH) could be due to conformational changes of the macromolecules and the cross-linking, herein, the most significant change of the viscosity seems to be due to the hydrophobic moiety (benzene ring) (Fig. 7). In addition, from a comparison with the modified xanthan solutions viscosity of the samples supernatants (Section 2.3) as a function of shear rate, it seems that the presence of DWCNTs particles reduces the viscosity of the system as shown on Fig. 8; hence, the presence of DWCNTs is associated to more pronounced shear thinning behavior. Overall, it is also obvious from the

viscosity measurements, especially at low shear rate, at 0.5%, that all the Xan derivatives/DWCNTs dispersions showed a strongly lower viscosity than samples of the three derivatives alone (Fig. 8(a-c)). Moreover, XEPH/DWCNTs showed lower viscosity than XPA/DWCNTs and XDPMA/DWCNTs which presented relatively similar profiles (Fig. 8d). However, according to  $\zeta$ -potential measurements (Fig. 4), samples of XPA and XDPMA showed  $\zeta$ -potential smaller than XEPH for pH above 5. Meanwhile, the hydrophobic interactions between the DWCNTs and the aromatic moiety through  $\pi$ - $\pi$  stacking are more pronounced in the case of XPA and XDPMA compared to XEPH, thus resulting in better disper-

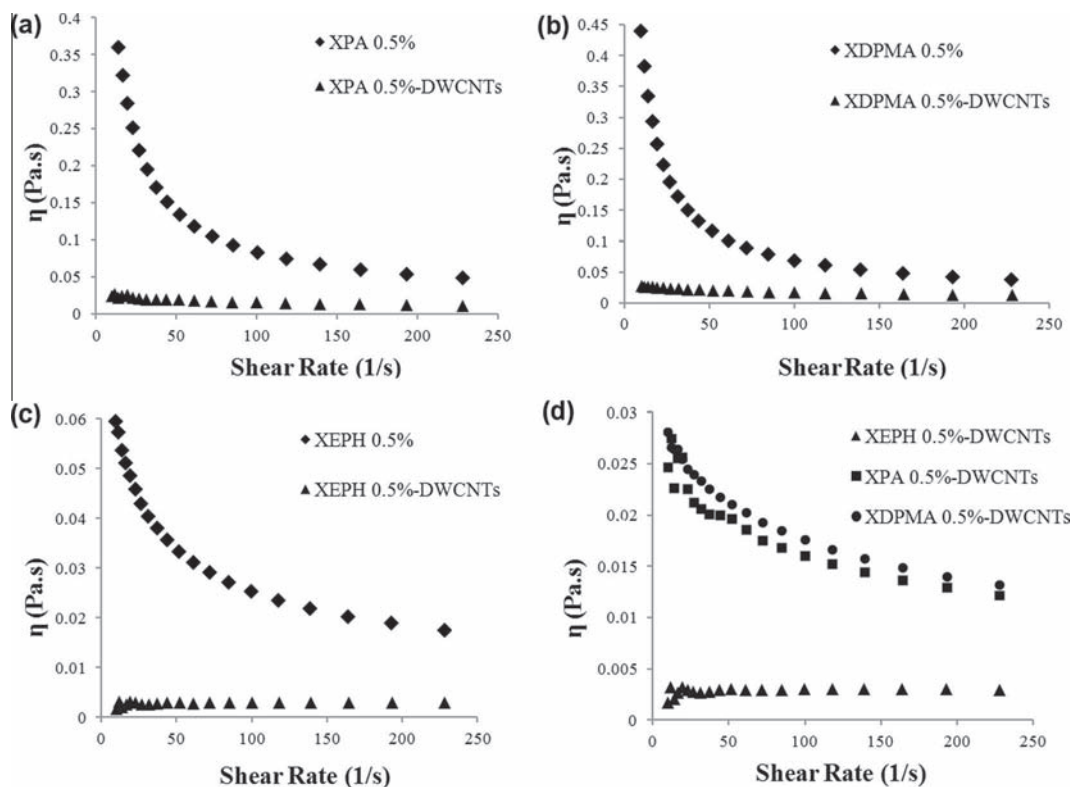


Fig. 8 – Plots of viscosity versus shear rate of DWCNTs suspensions at 25 °C, pH 7.

sions, as confirmed by the previous results by Liu et al. [59]. Finally, this effect can be interpreted in terms of the discrepancies in their chemical structures. Henceforth comparing the viscosity of samples, in all cases the solutions were shear thinning at all shear rates and the viscosity of DWCNTs-free samples is relatively higher. Consequently, DWCNTs are responsible for this effect, by acting as inter-molecular interactions (hydrophobic interactions) yielding therefore, conformational change of the macromolecules (Xan derivatives) of the continuous-phase. In order to disperse CNTs in water, hydrophobic tail groups orient themselves face toward the nanotubes surface while hydrophilic head groups extend into the water [14,15,61]. Hence, better charge repulsion between the hydrophilic groups of Xan derivatives prevents their agglomeration, and therefore a drop of viscosity is observed at low shear rate.

#### 4. Conclusion

In summary, DWCNTs have been successfully dispersed in aqueous media via non-covalent modification with new hydrophobically modified derivatives of Xanthan gum containing aromatic moieties. Our results show strong interactions between the modified derivatives and DWCNTs in water. The intensity of interactions depends especially on the chemical structure of the hydrophobic head. However, resulting suspensions of DWCNTs have quite a high stability against agglomeration resulting from the high hydrophobic interaction between the benzene ring and the tubes through  $\pi$ - $\pi$  stacking. Moreover, XPA and XDPMA confirm the successful immobilization of DWCNTs for very acidic media compared to XEPH. It was found that, above pH 5, the three derivatives allow obtaining stable suspensions. Thus, these results indicate that the introduction of an aromatic moiety into the backbone of Xanthan enhances the dispersibility of CNTs in water via  $\pi$ - $\pi$  stacking interaction; hence this non-covalent method may be beneficial to contribute for many CNTs applications. Moreover, these results also open interesting perspectives for the toxicity assessment of dispersed CNTs and we are currently investigating the use of our modified biopolymers in this context.

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