Combination of two dispersants as a valuable strategy to prepare improved poly(vinyl alcohol)/carbon nanotube composites

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ABSTRACT

We here present an effective strategy to prepare enhanced composites using poly(vinyl alcohol) (PVA) and multiwalled carbon nanotubes (MWCNT). It contains two essential steps. First, the elaboration of homogeneous aqueous MWCNT dispersions and the selection of the most effective dispersing agent. In a sequential dispersion protocol for seven common dispersants, including surfactants and polymers, the dispersion quality and dispersion ability, independent of the intrinsic nature of the dispersing agent were established using zeta-potential and UV-Vis-spectroscopy. Second, the combination of the most effective dispersing agent, namely dodecylbenzenesulfonate (SDBS) with a polymer dispersant of high affinity towards the PVA matrix, namely polyvinylpyrrolidone (PVP). This resulted in homogeneous PVA-MWCNT composites with significantly improved glass transition temperature by up to 12 ºC as a function of the sequential order of dispersant addition. The presented dispersion strategy is straightforward and thus may provide a fast, reliable and general guide for fabricating nanotube composites with improved performance.

Keywords: A. Nano composites, A. Carbon nanotubes, A. Polymers

1. Introduction

Carbon nanotubes (CNTs) have attracted increasing interest since their discovery due to their outstanding properties, including high moduli, high aspect ratio, and excellent thermal and electrical conductivities among others [1]. As fillers in polymers, nanotubes offer extraordinary advantages for

the development of new materials with improved properties [2, 3]. However important challenges still need to be resolved, including (i) homogeneous dispersion of CNTs in the polymer matrix, and (ii) establishment of a strong interfacial interaction/wetting between the CNTs and the matrix. Several approaches have been used to produce carbon nanotube-polymer composites with apparent homogeneous dispersion of the fillers, such us high power ultrasonic mixers [4], surfactants [5], solution mixing [6-10], and in situ polymerization [11]. Though, to-date, there has been no convincing transference of these CNT superior properties to the macro-structural level [12]. Chemical functionalization of the CNT surface [13, 14] has been proposed as a way to effectively disperse the nanotubes in the polymer matrix, and to promote interfacial interactions between CNT and polymers. However, this approach alters the π-electronic conjugation in CNTs, with the consequent deterioration of the unique CNT properties [15, 16]. For this reason, very frequently, non-covalent approaches are preferred. Consequently, solution mixing with addition of dispersants has been one of the most common methods used to overcome the problems associated with the nanotube aggregation. Following this approach a large number of CNT dispersants, both surfactants and polymers, have been reported [15-18]. Here, the nature of the dispersant, its concentration, and the type of interaction with nanotubes have been identified as key parameters for an optimal dispersion [15, 19]. Ionic surfactants are mostly selected to disperse CNTs for the preparation of composite materials, and frequently high surfactant concentrations are required to guarantee a good CNT dispersion. Unfortunately, due to the high surfactant content, the combination of the prepared CNT dispersions with the polymer matrices alters the processability of the resulting system and further optimization of the composite material is usually required. Acosta et al. [20] proposed the use of mixtures of anionic surfactants with cationic surfactants for improving the efficiency of the surfactants, and subsequent studies [21, 22] showed special synergism between anionic/cationic surfactants, which reduced the concentration of surfactant required to disperse CNTs. However, to the best of our knowledge, no preparation of composite materials with mixed surfactant CNT dispersions has been published. In this study, we propose a different approach, consisting on the use of a mixture of two dispersants of different nature: a surfactant with high efficiency in dispersing

CNTs, and a polymer dispersant of high chemical compatibility to PVA, as an efficient method to prepare improved poly(vinyl alcohol)/carbon nanotube composites. We also show that by adjusting the order of the dispersant addition, favorable interactions are established, resulting in a significant increase of glass transition temperature. Thus, the elaboration of pre-optimized MWCNT dispersions mixtures containing an ionic surfactant and a compatible polymer component is a valuable strategy to provide tailored MWCNT dispersions for fabricating MWCNT composites with superior characteristics.

2. Experimental

2.1. Materials

Commercial multi-walled carbon nanotubes (MWCNTs, type NC7000) kindly provided by Nanocyl S.A., were employed for this work. Four surfactants, namely sodium dodecylbenzenesulfonate (SDBS), lithium dodecylsulfate (LDS), hexadecyltrimethylammonium bromide (HAB), and octyl phenol ethoxylate (Triton X-100), and three polymer dispersants, namely Tween-60, Pluronic F68 and Polyvinylpyrrolidone (PVP) were purchased from Sigma-Aldrich and used without further purification. Polymer matrix: Poly(vinyl alcohol) (PVA) (Sigma Aldrich), with an average molecular weight (MW) of 146000 - 186000 g/mol was used as polymer matrix.

2.2. Preparation of CNT dispersions

For each dispersant, a progressive sequential protocol has been developed, consisting of several successive steps, in which only one dispersion parameter was varied, while the others were kept constant. Dispersant solutions were prepared dissolving the adequate amount of dispersant in distilled water until complete solution. The dispersions were obtained adding MWCNTs into the dispersant solution followed by ultrasonication with a high-power sonication tip processor (model Hielscher DRH-UP400S applying an output power of 250 W at an on-off cycle frequency of 12 kHz). Dispersions were centrifuged and supernatants decanted for further analysis. In case of dispersant mixtures: the first dispersant was dissolved in water and the required amount of MWCNTs was added employing the optimized conditions for the first dispersant. Subsequently, the

second dispersant was added under the optimized conditions for the second dispersant. This resulted in a homogeneous and stable dispersion.

2.3. Characterization of the dispersions

Zeta potential and particle sizing (hydrodynamic radius) measurements of MWCNT aqueous dilute dispersions were carried out with a Malvern Zetasizer Nano system (UK) with irradiation from a 633 nm He-Ne laser. If not otherwise stated, all measurements were performed at a controlled temperature of 25 ºC and repeated 5 times for each type of dispersion. This technique is based on dynamic light scattering, and calculates the zeta potential by measuring the electrophoretic mobility, μ, using the Smoluchowski approximation [23], $\mu= \varsigma\varepsilon_m V/4\pi\eta D$, where V is the applied voltage, η is the solution viscosity, ε_m is the dielectric constant of the medium, and D is the electrode separation (in SI units). This approximation is rigorously valid only for spherical particles, and may overestimate in some cases the actual zeta potential [24]. Nevertheless it has been successfully applied to nanotube dispersions to qualitatively understand the influence of the surface charge on dispersion quality [25, 26]. Furthermore, it is worthwhile mentioning that the resulting "particle" dimensions from this type of measurements refer to the hydrodynamic diameter of spherical objects. In the case of dispersed MWCNTs these are conceptually understood in terms of a "particle sphere" composed by aggregated MWCNTs. UV-Vis absorbance was recorded on a Shimadzu U2401-PC spectrometer. Concentration of MWCNTs, before and after centrifugation, was calculated from the absorbance at a fixed wavelength (660 nm) in order to determine the fraction of aggregates removed by centrifugation.

2.4. Composite preparation and characterization

Poly(vinyl alcohol) (PVA) reinforced composites were prepared by dissolving a controlled amount of PVA in distilled water. Once the PVA was completely dissolved the necessary volume of the analyzed dispersions were incorporated to obtain different loadings of MWCNT (0.1 to 2 wt. % with respect to PVA). The corresponding solution was mixed with a magnetic stirrer during at least 30 min. MWCNT/PVA nanocomposites films were obtained by drop casting and further characterized.

Glass transition temperatures (T_g) of the prepared composites were determined by differential scanning calorimetry (DSC). A Mettler DSC-823E apparatus calibrated using an indium standard (heat flow calibration) and an indium-lead-zinc standard (temperature calibration) was used. Dynamic heating was performed from room temperature to 200 ºC at a rate of 20 ºC/min to 10 mg of sample (exactly weighted) placed into standard 40 mL aluminum crucibles, under a 100 mL/min flow of nitrogen. The glass transition temperature (T_g) was taken as the inflection point of the heating DSC traces. The morphology of the composite films and the formation of aggregates and their distribution was probed by optical microscopy (Zeiss AX10).

3. Results and discussion

3.1. Dispersion optimization using zeta potential and average particle size

The aim of this work is to prepare enhanced composite materials based on a water-soluble polymer matrix, PVA, and MWCNT using a combination of two surfactants. To this end, first we have developed a sequential dispersion protocol to ensure an effective MWCNT dispersion. Seven common dispersants were used in this work and the dispersion conditions for each dispersant adjusted to achieve an optimal dispersion quality for each case. This refers to the stability of the dispersions with respect to MWCNT concentration and the formation of MWCNT aggregation. The criteria for the dispersion stability are established from zeta-potential and average particle size measurements under different environmental conditions. This is completed by UV-Vis spectroscopy in order to provide a classification of the dispersing ability of the different dispersants, independent of their intrinsic nature.

The initial step of the study relates to the determination of the optimum MWCNT/dispersant ratio. Thereto we used a fixed concentration of MWCNTs (1mg/mL), and a variable dispersant concentration (0.5, 1, 2, 5, 10, and 20 mg/mL). All dispersions were prepared using the following initial conditions: sonication for 15 min and centrifugation at 3500 rpm for 30 min. Zeta-potential and particle size measurements were performed in order to assess the quality of the dispersions. Fig. 1a shows the zeta-potential and particle size values for the dispersions obtained with increasing SDBS concentration. The zeta-potential is high for all the assayed concentrations, and increased with

SDBS concentration reaching -53 mV at 20 mg/mL of SDBS, clear indication of the high dispersion stability achieved with this surfactant. It is widely accepted that stable dispersions are obtained when the absolute value of the zeta potential is larger than 15 mV [27]. At these conditions the smaller particle sizes also underline good dispersion quality, despite the fact that this parameter barely varies with SDBS concentration.

Next, the effect of the centrifugation was evaluated, and dispersions at different centrifugation speeds (1000, 3500, 5000, and 10000 rpm) were prepared, keeping the rest of parameters constant: MWCNT concentration (1mg/mL), sonication (15 min), SDBS concentration (20mg/mL, optimized in the former step). Fig. 1b shows the particle size and zeta potential values for these experiments. No clear tendency was observed for both parameters, indicating similar stabilities for all the studied conditions. We chose 5000 rpm as the best compromise between stable MWCNT dispersions and adequate final nanotube concentration. Subsequently, the sonication time was analyzed for the dispersion process. Dispersions of MWCNTs (1mg/mL) with SDBS (20 mg/mL) were prepared at different ultrasonication times (5, 15, 30, 60 minutes). All the dispersions were centrifuged at 5000 rpm for 30 min. The light scattering analysis (Fig. 1c) shows a small increase of zeta potential and decrease of particle size with sonication time. Sonication time of 30 minutes was chosen for SDBS dispersions since longer sonication times do not result in further improvement of the dispersion quality. The fact that neither centrifugation nor sonication essentially affect zeta potential and particle size underlines that the critical factors are rather related to finding an adequate surfactant and concentration range.

Dispersions with different nanotube concentrations (0.25 to 2 mg/mL) were also prepared. The optimal conditions for SDBS were applied, and results from the dynamic light scattering analysis collected in Table S1 (see Supplementary materials). Absolute values of the zeta–potential increased with nanotube concentration, up to 55 ± 2 mV at a MWCNT concentration of 2 mg/mL. On the contrary, particle size increases with MWCNT concentration for concentrations above 1 mg/mL, resulting in formation of visible aggregates that may negatively influence the quality of the dispersion. Thus we established an upper MWCNT concentration limit of 1mg/mL for which stable

dispersions of MWCNTs can be achieved using SDBS as surfactant. Higher nanotube concentrations will require further optimization effort.

The stability with pH and temperature of the optimized dispersions was also monitored (see Fig. S1, Supplementary materials), and results indicate high dispersion stability in a wide range of pH (3-10) and temperature (2 to 50 ºC).

An identical protocol was applied for all the dispersants detailed in the experimental section, and the optimal conditions established for each one are summarized in Table 1.

At this point the obtained results can be summarized as follows: i) Absolute zeta potential values significantly higher than 15 mV were obtained for all the used dispersants, underlining the excellent dispersion stability achieved by applying our progressive sequential protocol. ii) Average particle sizes around 200 nm were found for most dispersants. Only polymer dispersants show significantly larger particle sizes and lower zeta potentials. iii) Different dispersant/MWCNT ratios and sonication times were obtained for all systems. iv) Centrifugation speed was found to have little effect on light scattering parameters. v) Optimal dispersion conditions were established for MWCNT concentrations up to 1 mg/mL. Larger aggregates were visible at higher concentrations. Thus, further optimization at these concentrations becomes necessary. vi) Optimal dispersion conditions elaborated for one dispersant do not necessary apply for another dispersant. vii) Order of dispersing ability according to light scattering techniques: For surfactants: SDBS≈HAB > LDS > Triton X-100. For polymer dispersants: PVP > Pluronic F-68 > Tween-60.

As a next step we analyzed the stability of the optimized aqueous MWCNT dispersions over time. During the period of one month we measured the zeta-potential and average size in order to evaluate the dispersion stability. Surprisingly, both values showed very little variation over time. After one month, zeta-potential value changed from -55 ± 2 mV to -52 ± 2 mV, and average particle size showed no significant differences (180 ± 5 nm); additionally, no visible aggregates were observed during this period. These results show that by applying a progressive optimization protocol using dynamic light scattering parameters (zeta-potential and average particle size) as criteria for the

dispersion quality stable aqueous dispersions of MWCNTs with different dispersants can be successfully elaborated.

3.2. Classification of dispersing ability of dispersants using UV-Vis absorption spectroscopy

Although dynamic light scattering is a valuable tool for assessing the stability of aqueous MWCNT dispersions, this technique does not allow a direct comparison of the dispersion ability of dispersants of different nature. While excellent MWCNT dispersions can be obtained with both, surfactants and polymer dispersants, the polymer systems usually exhibit lower zeta potentials and larger particles sizes. In order to classify the dispersing ability of dispersants independent of their intrinsic nature, dynamic light scattering measurements were complemented by performing UV-Vis absorption spectroscopy on MWCNT dispersions.

Assessing nanotube dispersion quality by UV-Vis spectroscopy is based on the assumption that beyond 300 nm (a) the employed dispersants do not contribute to the UV-Vis absorption, and (b) any remaining absorption is linked to the presence of dispersed nanotubes. In the case of single-walled carbon nanotubes the presence of specific Van-Hove singularities between 630 and 660 nm facilitates a quantitative evaluation of the dispersion quality by UV-Vis spectroscopy [17, 25, 28]. However, this methodology can be equally employed for MWCNT dispersions, which are characterized by a featureless absorption in the above mentioned wavelength range. Thereto we measured the absorbance of the various optimized MWCNT dispersions at 660 nm for different MWCNT concentrations before and after applying an additional centrifugation step. For all the employed dispersants the absorbance data linearly increase with the MWCNT concentration over the whole concentration range assayed. Thus, eventually existing aggregates must have absorption coefficients similar to those of dispersed MWCNTs. Linear fits and application of Lambert-Beer provided values for the apparent molar extinction coefficient (ε) for MWCNTs.

An extinction coefficient of 3947 mLmg^{-1}m^{-1} was obtained for the dispersion with SDBS, in good agreement with the reported ε values for SWCNTs, ranging from 3000 to 4000 mLmg^{-1}m^{-1} [29, 30]. Different molar extinction coefficients for MWCNTs were obtained for each dispersion system, indicating different dispersion abilities for each dispersant. A higher extinction coefficient usually

points to improved dispersion quality attributed to the disaggregation of nanotube bundles or an enhanced presence of individual nanotubes [30]. Considering the molar extinction coefficient as a parameter to define the dispersion quality the following trend was established: SDBS > HAB > Tween 60 > LDS ≈ Pluronic > PVP > Triton X-100. With respect to the surfactants, the trend is coincident with the one observed by light scattering analysis, indicating that both techniques are adequate to define quality of nanotube dispersion for this type of dispersants. However, polymer dispersants exhibit a different trend than the one observed by light scattering. Since the absorption data from UV-Vis measurements are independent of the type of dispersant (they do not contribute to the absorption at 660 nm) this technique thus should provide a reliable measure for comparing surfactants with polymer dispersants, i.e. dispersants of different intrinsic nature. Parameters like different molecular size of the polymer, and different ionic character (most times non-ionic, therefore non-charged) may have more weight on the obtained values of zeta potential, and average particle size than on the dispersion ability. Nevertheless, for our progressive sequential protocol, light scattering measurements have proven to be a fast and effective method to assess the quality of MWCNT dispersions.

Additional information can also be extracted from the UV-Vis analysis by studying dispersions after centrifugation. Lower absorption values, compared to the ones obtained for the non-centrifuged samples, were obtained, indicating removal of aggregates by centrifugation. Moreover, the difference on absorbance values, before and after centrifugation, became more significant at increasing nanotube concentration. In the case of SDBS, both absorption values are almost coincident for nanotube concentrations up to 0.05 mg/mL (Fig. 2). This clearly reveals a high stability of the nanotube dispersion and a reduced presence of aggregates at this concentration range, otherwise the centrifuged dispersion would exhibit much lower absorbance. On the other hand, for Triton X-100 the absorption values diverge above 0.025 mg/mL (Fig. 2), indicating larger amounts of aggregates removed by centrifugation beyond this MWCNT concentration.

We have used this information to define the "dispersion limit" of the dispersant, i.e. the nanotube concentration above which larger aggregates, removable by centrifugation, can be detected (see

Table S2 in Supplementary materials). Two groups could be distinguished with respect to the dispersion limit: (a) SDBS, HAB, Tween 60 and Pluronic, with dispersion limits above 0.05 mg/mL, and 2) dispersants such as LDS, PVP, and Triton X-100 with dispersion limits below 0.025 mg/mL. Calculating now the fraction of aggregates removed by centrifugation according to Equation (1) [28],

$$\chi_{agg} = (ABC - AAC)/ABC, \qquad\qquad (1)$$

where ABC and AAC define the absorbance at $\lambda = 660$ nm before and after centrifugation, respectively, and plotting χ_{agg} versus the initial MWCNT concentration (Fig. 2), we can be clearly seen that the SDBS dispersion, over the whole MWCNT concentration range, contains the lowest amount of aggregates being indicative of its high dispersing ability. With the highest number of aggregates over the whole MWCNT concentration range, the lowest dispersion ability is established for Triton X100. Finally, it is worth to mention here that the amount of aggregates observed for all our dispersions is lower than the one found for single-walled carbon nanotubes [30], which once more underlines the efficiency of our dispersion methodology.

3.3. Preparation of PVA composites

In the previous sections, we have shown that stable aqueous MWCNT dispersions can be successfully prepared, and their dispersion degree quantified by light scattering, and UV-vis spectroscopy techniques. The latter technique has allowed us to classify dispersants according their ability to produce stable nanotube dispersions independent of their nature. In the following, in order to demonstrate the benefits of applying the developed sequential protocol, we study the preparation of composites based on water-soluble poly(vinyl alcohol) as polymer matrix and optimized aqueous MWCNT dispersions. Two types of MWCNT dispersants were used: SDBS, chosen among all the surfactants for its high MWCNT dispersing ability and PVP with good chemical compatibility to PVA which should contribute to enhanced interactions between MWCNTs and the PVA matrix. Four series of MWCNT dispersions were prepared: (1) MWCNT/SDBS, with SDBS as dispersant, (2) MWCNT/PVP with PVP as dispersant, (3) MWCNT/SDBS+PVP dispersing first the nanotubes with SDBS, and then with PVP, and (4) MWCNT/PVP+SDBS, adding the dispersants in inverse

order to the nanotubes, i.e. first PVP, and second SDBS. We applied the sequential protocol developed in previous sections to prepare the four MWCNT dispersions, which were also characterized by measuring their zeta-potential and average size. Results are summarized in Table 1.

Mono-dispersant dispersions exhibited the characteristics previously described. SDBS, with a better dispersion performance, produced dispersions with smaller average particle size and higher zeta-potential, and PVP larger particle sizes and lower zeta-potential values. When PVP was used in combination with SDBS no significant changes in the average size with respect to the SDBS dispersions were observed, indicating that no aggregation occurred and the stability of the dispersions was maintained. On the other side lower absolute values of the zeta-potential were observed when PVP was used. However, the dispersions were maintained for long periods of time without sedimentation or aggregation, indicating their high stability. Interestingly, for dispersant mixtures the order of dispersant addition apparently, had no influence on the dispersion quality, and both dispersion mixtures showed acceptable quality, according their zeta-potential, and particle size values.

Subsequently, the four different MWCNT dispersions were used to prepare MWCNT/PVA composites with MWCNT loadings from 0.1 to 2 wt. % with respect to PVA. Composites were analyzed by differential scanning calorimetry, and the effect of the MWCNTs estimated from the polymer T_g values, is shown in Fig. 3. The evaluation of the T_g values of the composites provides us with an indirect and fast method to determine both the dispersion and the effective transference of properties from the MWCNTs to the polymeric matrix. The T_g value of the neat PVA was determined to be approximately 75 °C. Blank samples of PVA containing only SDBS and PVP showed no significant differences in the T_g values. Composites prepared with MWCNT/SDBS dispersions showed similar T_g to the original PVA, independent of the MWCNT content, indicative of a low enhancing effect of nanotubes on the composite, in spite of the high quality dispersions obtained with this surfactant. A slight increase of the T_g for MWCNT loadings above 1 wt. % was observed when PVP was the dispersant. Importantly, mixtures of dispersants lead to notable enhancement of the composite characteristics with respect to the mono-dispersant systems. Here the

order of dispersant addition certainly had a significant influence on the final composite properties. Although both dispersant mixtures showed similar dispersion quality, addition of SDBS first, followed by PVP resulted in a significant increase of T_g up to 87 ºC for composites loaded with 2 wt. % of MWCNTs. Choi et al. described in their study [31] an increase of 6 ºC in the T_g values of PVA reinforced with 2 wt. % of MWCNTs. Our results point to an improved integration and dispersion of MWCNTs through the polymer matrix when surfactant/polymer dispersion mixtures are used. While SDBS favors a high degree of MWCNT dispersion in the PVA matrix the presence of PVP in the outer layer of the dispersed MWCNTs is ultimately responsible for efficient transfer of properties from the MWCNTs to the polymer matrix. Although the sizes of the aggregated MWCNTs in dispersions are in the range of 200 nm, in the composites, the PVA polymer chains easily may diffuse into the MWCNT aggregates and establish proper nanoscale interactions. The efficiency of this process depends on the compatibility of the dispersants with the polymer matrix.

Optical microscopy of the MWCNT/PVA composite films for the different dispersants at a fixed MWCNT loading fractions of 0.5 wt. % illustrates this situation (Fig. 4). The appearance of homogeneously distributed 1 μm-sized "dot-like" objects in the PVA composites, typically observed when SDBS dispersant is present and in direct contact with PVA, indicates the formation of self-associated structures (micelles) in the composite. However, when PVP dispersant is present and in direct contact with PVA dot-like structures do not form and a rather smooth composite morphology is observed. When MWCNT-containing mixtures of SDBS and PVP are used it becomes evident that the composite morphology is influenced by the "second" i.e. "outer" dispersant layer covering the MWCNTs and thus by the sequence order for mixing the two dispersants: MWCNTs dispersed in PVP and mixed with SDBS show the 1 μm "dot-like" morphology typical for SDBS in contact with PVA. On the contrary, MWCNTs dispersed in SDBS and mixed with PVP show the smooth morphology typical for PVP in contact with PVA. Thus, optical microscopy, in combination with the results form DSC measurements provides the following conclusions: (a) SDBS homogeneously disperses MWCNTs, (b) PVP acts as an efficient coating layer on the well-dispersed SDBS-covered MWCNTs, and (c) the PVP coating layer on the SDBS-covered MWCNTs provides a high

compatibility with the PVA matrix characterized by a smooth composite morphology, free of dot-like aggregates, favoring effective interaction with the PVA matrix as expressed by an enhanced glass transition temperature. These observations point out the important role of the outer layer. It defines the appearance in optical microscopy and it is accountable for an effective transfer of MWCNT properties to the polymer matrix. On the contrary, the inner layer apparently is responsible for the dispersion degree of MWCNTs in the matrix system. MWCNT dispersion mixtures consisting of a surfactant, providing a high MWCNT dispersion degree, to which a polymer dispersant compatible with a given polymer matrix system is added thus is a highly efficient strategy to elaborate tailored aqueous MWCNT dispersions. Once incorporated into the polymer matrix, a corresponding homogeneous MWCNT composite with enhanced properties is obtained.

4. Conclusions

We have developed tailored MWCNT dispersions based on a combination of a surfactant and a polymeric dispersing agent to obtain MWCNT/PVA composites with enhanced thermal properties. A significant increase of the glass transition temperature of PVA by 12 °C has been achieved using a loading fraction of only 2 wt% of MWCNT, well dispersed in a mixture of SDBS-PVP. While SDBS alone appeared as the most efficient dispersing agent in the PVA matrix it did not result in the enhancement of its properties. However, SDBS in combination with PVP, facilitated the additional interaction between matrix and MWCNTs and improvement of its properties. Thus, the approach towards improved composites contains two essential steps: First, establishing for a given nanotube system the most efficient dispersant in a progressive sequential protocol with the help of zeta-potential and UV-Vis spectroscopy. Second, choosing an additional dispersant with a high affinity to the polymer matrix in question and combine it with the selected dispersing agent in an sequential order that allows establishing efficient transfer of properties between nanotubes and a given polymer matrix. The presented dispersion strategy is straightforward and thus may provide a fast, reliable and general guide for fabricating nanotube composites with improved performance.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found on pages 21-23.

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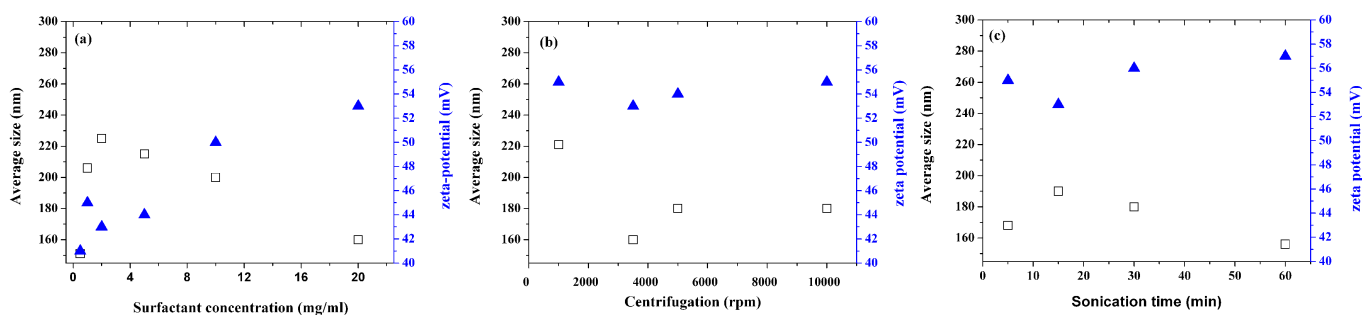
Fig. 1. Average size and zeta- potential of the MWCNT dispersions prepared with SDBS. (a) effect of SDBS concentration, (b) effect of centrifugation process and (c) effect of sonication time. Zeta potential and particle sizes are indicated by ▲ and □, respectively.
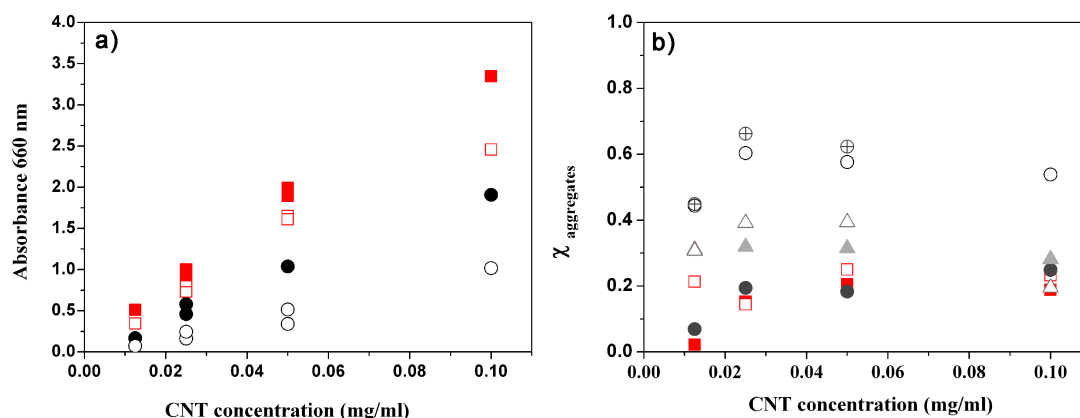
Fig. 2. (a) UV Vis absorption at 660 nm vs. MWCNT concentration of optimized dispersions: SDBS (■ before, □ after centrifugation); Triton X-100 (● before, ○ after centrifugation). (b) Content of aggregates in MWCNT aqueous dispersions for different dispersants. Individual dispersants are indicated by the following symbols: ■ SDBS, ● Pluronic, □ Tween 60, ▲ LDS, △ HAB, ○ PVP and ⊕ Triton X-100.
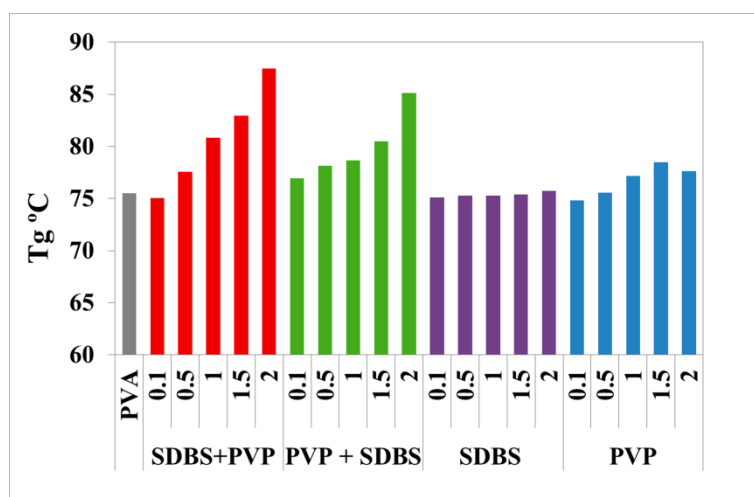
Fig. 3. Representation of the T_g values of the PVA/MWCNT composites obtained using as dispersants SDBS and PVP, and mixtures thereof. Numbers refer to the used MWCNT concentration.
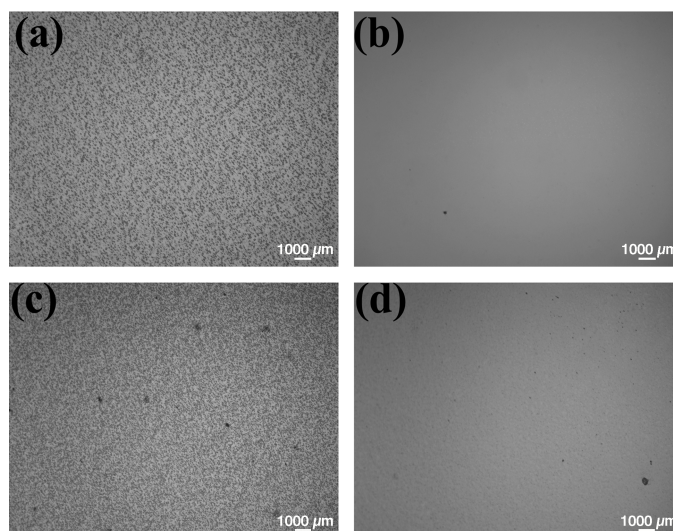
Fig. 4. Optical microscopy images of PVA/MWCNT composites at MWCNT loading of 0.5 wt% for different dispersants: (a) SBDS, (b) PVP, (c) PVP-SDBS, and (d) SDBS-PVP.

Table 1. Conditions for optimized MWCNT dispersions for all dispersants and mixtures.

Surfactant	MWCNT conc. (mg/mL)	Surfactant conc. (mg/mL)	Sonication time (min)	Centrifugation speed (rpm)	Average size (nm)	Zeta-potential (mV)
SDBS	1	20	30	5000	160 ± 5	-55 ± 2
Triton X-100	1	1	5	10000	180 ± 6	-30 ± 1
HAB	1	5	15	5000	180 ± 5	60 ± 4
LDS	1	10	15	5000	200 ± 6	-54 ± 3
Tween-60	1	10	15	5000	221 ± 20	-15 ± 2
Pluronic F-68	1	5	15	5000	235 ± 6	-20 ± 5
PVP	1	5	15	5000	300 ± 11	-25 ± 3
[*]SDBS/PVP	1/0	20/5	30/15	5000/5000	166 ± 1	-14 ± 1
[*]PVP/SDBS	1/0	5/20	15/30	5000/5000	186 ± 8	-16 ± 1

[*]For mixtures: The first component refers to an aqueous dispersion containing MWCNTs prepared according to the optimized conditions for the corresponding dispersant (first value). The second component refers the second dispersant added to the prepared MWCNT dispersion according to the optimized conditions for the second dispersant (second value).

Combination of two dispersants as a valuable strategy to prepare improved Poly(vinyl alcohol)/carbon nanotube composites

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Particle size and zeta potential for MWCNT dispersions prepared with SDBS in a concentration range ranging from 0.25 to 2 mg/mL

Table S1. Effect of the MWCNT concentration on average size and zeta-potential of the MWCNT dispersions prepared with SDBS under the optimal conditions established.

MWCNT conc. (mg/mL)	Particle size (nm)	Zeta potential (mV)
0.25	240	-46
0.5	160	-51
1	160	-55
2	280	-55

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Average size and zeta-potential at different pH values and temperatures
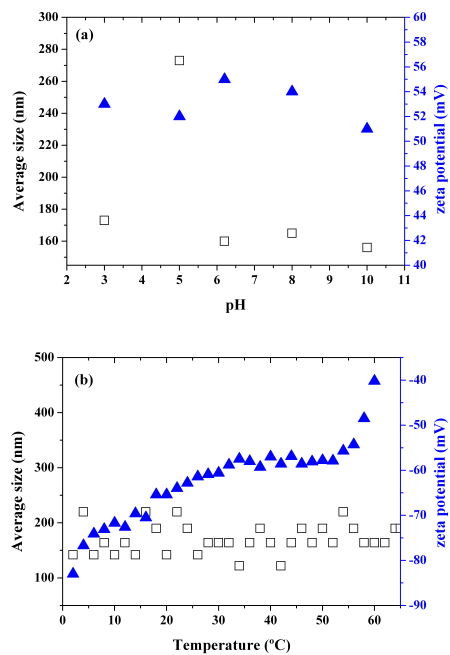
Figure S1. Average size and zeta-potential of the optimal MWCNT dispersions obtained with SDBS a) at different pH values and b) effect of temperature. Zeta potential and particle sizes are indicated by ▲ and □, respectively.

Fig. S1 shows the variation of average size and zeta-potential of the optimal MWCNT dispersions obtained with SDBS with pH and Temperature. Zeta potential exhibits a slight increase with pH, being the highest absolute value of zeta potential found at pH = 6. Smaller particles are also obtained at this pH and beyond, indicating enhanced dispersion stability in neutral to alkaline range, as can be expected from the anionic character of the surfactant. However, the high zeta-potentials values measured are indicative of good dispersion stability over the whole pH range from 3 to 10. In what concerns the temperature, the stability of the dispersion increases as the temperature decreases from 65 to 2 ºC, being -85 mV the highest zeta potential found (at 2 ºC). The low mobility of the dispersed MWCNTs at low temperature ensures a good stability. At high temperatures the mobility increases and leads to an enhanced number of collisions among MWCNTs. This results in larger

nanotube aggregates, which tend to precipitate. Consequently, less stable dispersions are obtained at elevated temperatures.

Nevertheless, at the highest temperature assayed (65 ºC) the zeta-potential with a value of -40 mV still indicates a very good MWCNT dispersion degree. For the temperature range between 20 and 50 ºC values for zeta- potential and particle size remain almost constant underlining high dispersion stability for this important working range.

Extinction coefficients and dispersion limits for the used dispersants

Table S2. Extinction coefficients and dispersion limits for all dispersions prepared.

Surfactant	ε (mL/mg/m)	Dispersion limit (mg/mL)
SDBS	3947	0.05
TRITON X-100	1599	0.025
HAB	3287	0.05
LDS	2938	0.025
TWEEN-60	3184	0.05
PLURONIC F-68	2915	0.05
PVP	2274	0.025