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Finest nanocomposite films from carbon nanotubes-loaded poly(methyl methacrylate) nanoparticles obtained by Ouzo effect

Patrice Lucas,^{a,b} Malvina Vaysse,^{a,b} Julien Aubry,^a David Mariot,^a Rodolphe Sonnier^c and François Ganachaud,^{*a}

Composite particles, i.e. PMMA nanoparticles trapping one to few nanotubes in their core, were prepared by a derivative process of the solvent shifting technique, also called “Ouzo effect”. Particles were converted by simple annealing into films, of which thermal resistance was evidenced by microcalorimetry and thermogravimetry.

Since their discovery in the early nineties,¹ carbon nanotubes (CNTs) have been the subject of numerous researches, owing to the combination of electric, mechanical, thermal and chemical properties.² The CNTs’ large Van der Waals force density, wide interaction surface, long tubular geometry and low rigidity however favour their strong aggregation into bundles.³ One major challenge remaining to be solved today thus lies in obtaining the best dispersions, particularly in polymer matrices, to take advantage of their outstanding intrinsic properties. Nanotube surface functionalization,⁴ or co-extrusion with polymers⁵ generally allows yielding satisfying composite mixture. However, such techniques generally weaken the strength and / or reduce the size of the nanotubes.⁶

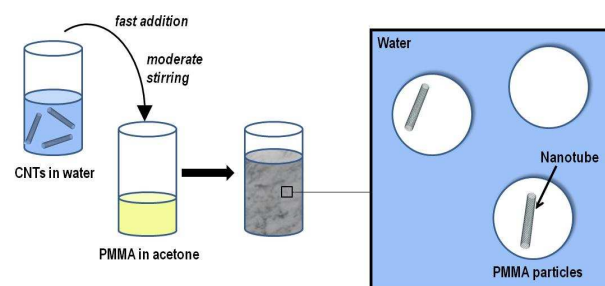
Recently, different techniques starting from aqueous dispersions of nanotubes have been proposed to prepare CNTs/polymer composites. CNTs aqueous dispersions were obtained by wrapping them with polyelectrolytes or by adding conventional surfactants; since there are no needs for chemical or mechanical inputs (apart from reasonable sonication to help at the dispersion), most CNTs retain their original shape and length.⁷ The ‘latex technology’ consists in mixing together 1/an aqueous dispersion of surfactant-stabilized CNTs and 2/ a polymer latex stabilized with the same surfactant. Removing water by different means (e.g. lyophilisation) leads to a nanocomposite.⁸ In some very specific instances, the latex was generated by in-situ polymerization of a monomer emulsion in presence of CNTs dispersions.⁹ The ‘coagulation technique’ described by Winey et coll.¹⁰ consists in co-precipitating in a non-solvent (typically water) a mixture of polymer (PMMA or PS) and carbon nanotubes preliminary dissolved in a common solvent, typically DMF. The difficulty here lies in the mixing of both solutes in the solvent while keeping a low viscosity solution, compulsory to safely mix both organic and aqueous phases during the coagulation step.

We propose in this communication a different and simpler

approach, called “polymer emulsification-coagulation” technique (PEC), a combination of the two techniques previously described.

It consists in nanoprecipitating a polymer solution in an aqueous dispersion of carbon nanotubes in tailored conditions so that the polymer traps the nanotubes into nanoparticles (Scheme 1). The number of CNTs entrapped in the nanoparticles (of typically 200 nm in size) ranges from 0 to 5 maximum, thus avoiding bundling of these (Figure S1). The final CNTs-loaded polymer nanoparticles can be stored into powder and melt to generate nanocomposite films or materials. The outstanding dispersion of CNTs into the polymer matrix is similar to the aqueous dispersion the nanocomposite arose from (1 to 1 copy). The following communication describes the concept of PEC technique, the resulting nanocomposite particles and films and some resulting thermal properties improvements.

The nanoprecipitation process is a general method to generate surfactant-free nanosized polymer particles. The spontaneous emulsification via solvent shifting technique (so-called « Ouzo effect »¹¹) requires to select a solvent and a non-solvent of the polymer which are fully miscible, and to track out concentrations where only nanoparticles are formed.¹² In the open literature, surfactant-free biodegradable polymer pseudolatexes are generated in a view of drug vectorization applications.¹³ The entrapment of water-dispersed solutes using this technique is however, to our knowledge, not widespread. We could only track one article where indomethacin-loaded magnetic particles were generated by nanoprecipitation in the presence of magnetite nanoparticles.¹⁴ In the course of a fundamental study on the nanoprecipitation of a model polymer,¹⁵ we previously derived a phase diagram for the PMMA/acetone/water system (Figure 1).



Scheme 1. Principle of entrapment of CNTs by the Ouzo-effect driven nanoprecipitation technique.

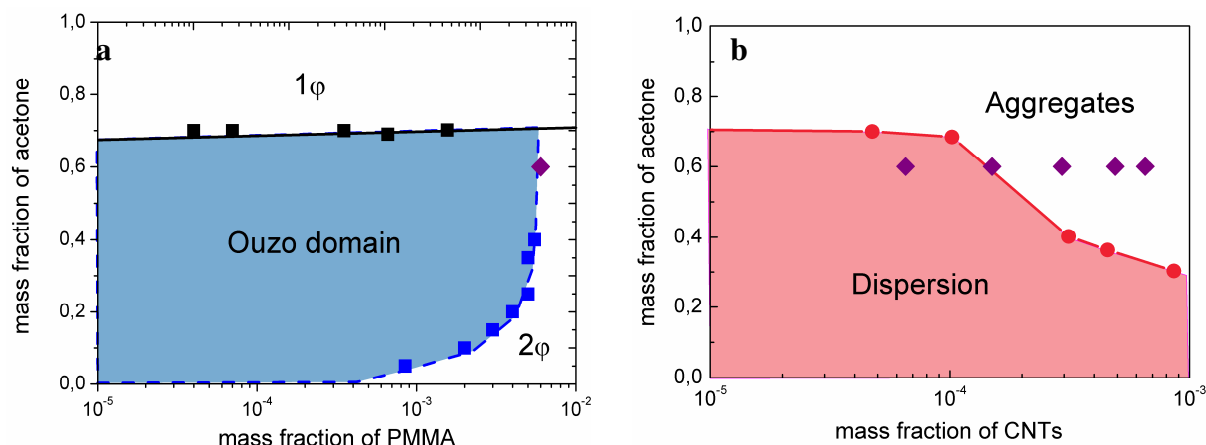


Fig.1 Binary phase diagrams showing the weight content of solvent (y axis) as a function of weight content of solute, PMMA (Fig. 1a) or CNTs (Fig. 1b) (x axis in log scale). The weight content of water is deduced from the other two values. The PMMA nanoprecipitation domain, depicted in blue, shows two characteristic limits: the binodal curve as a black line, best fit of black squares, and the Ouzo limit in blue dashed curve, best fit of the blue squares. CNTs dispersion stability domain, in pink, is delimited by the stability limit (red line deduced from red circles data). In both phase diagrams, the purple diamonds give the theoretical final mass fraction of solute (PMMA and CNTs) tested in this study (see actual values in Table 1 and text for details).

Two limits were experimentally derived on the polymer binary diagram in Fig. 1a (the content of water is deduced from solvent and polymer weight ratios): the *binodal* or *trouble point* curve, which separates the domain where the polymer is miscible in the mixture of solvent/nonsolvent (noted as 1 ϕ in the phase diagram) from the domain where it demixes; and the *Ouzo limit*, which separates the domain where nanoparticles are exclusively formed (Ouzo zone in blue, Figure 1a), from those where solvent-filled lumps are also generated (noted 2 ϕ in Figure 1; see ref. 14 for TEM photos). On Figure 1, we also reported on the second phase diagram the stability zone of aqueous dispersions of carbon nanotubes stabilized here by sodium cholate, one of the best dispersing agent of CNTs. Below the red line on Figure 1b, CNTs dispersions remain stable for at least an hour (pink zone in Figure 1b).¹⁶ For diluted enough s dispersions in water (typically below 10^{-5} in wt fraction), large contents of acetone (above 65% in wt.) are needed to provoke a rapid disrupting of the s dispersion. The purple diamonds represent theoretical final mass fractions of PMMA and CNTs in case of ideal composite formation (quantitative recovering of composite particles, 100% CNTs encapsulation). The actual results for these different formulations are given in Table 1 (*vide infra*).

Figure 2 gives an overview of TEM and SEM photos of original nanocomposite particles and of films resulting from particles annealing (120°C, 30 min.). Not all particles entrapped a single CNT (white arrow, Figure 2a): this explains the polydispersity of particles shapes observed using SEM (Figure 2b). Some CNT protrude from particles as stressed by black arrows on a zoom photo (Figure 2c). Final dispersion of the CNTs in annealed films is remarkable, without any evidences of bundles in the sample (the entire surface was screened during analysis). Such dispersion cannot, to our knowledge, be achieved nowadays by using other techniques. It was also observed that increasing the final

CNTs/polymer ratio enabled the encapsulation of a few CNT in a same particle, still without aggregating them, or nanotubes protruding from two or more particles (see TEM photos in Figures S1 and S2, respectively).

Different experimental conditions which enabled us to generate large contents of nanocomposites are given in the supporting information section. We were able to generate nanocomposite particles at any solvent final weight ratio ranging from 0.2 to 0.6. It is worth noting that if the solvent is quickly removed right after nanoprecipitation, it not only concentrates the dispersion, but also favors a longer stability of the dispersion (in the range of hours). It was observed that the final particle size increases while increasing the final weight ratio of solvent and/or while increasing the final content of polymers. pH of the aqueous dispersion has also a huge influence on the system. High contents of hydroxide ions favor the generation of small colloiddally stable PMMA particles at polymer weight ratio as high as 0.1.

The selection of surfactant to stabilize the CNTs dispersion is even more crucial in this process, since the 1:1 copy strategy entails that the CNTs aqueous dispersions be the finest prior to PMMA entrapment. Sodium dodecylbenzene sulfonate (NaDBBS), another common surfactant for CNTs, was likely used but did not lead to fine nanocomposites. Indeed, although the stability of the CNTs dispersion was found better than for those stabilized by cholate surfactant (see Figure S3), we were not able to destroy all CNTs bundles (which showed up on TEM photos: Figure S4). The limited entrapment of NaDBBS-stabilized CNTs into PMMA is obvious while centrifuging final composite particles, where a clear supernatant is the signature of 100% entrapment (Figure S5). The reason lies in the fact that the large bundles of CNTs cannot be trapped by the nanoparticles.

Table 1 summarizes different experiments where the CNTs loadings were varied. The final yield in composite nanoparticles (obtained after filtration, see experimental part for details)

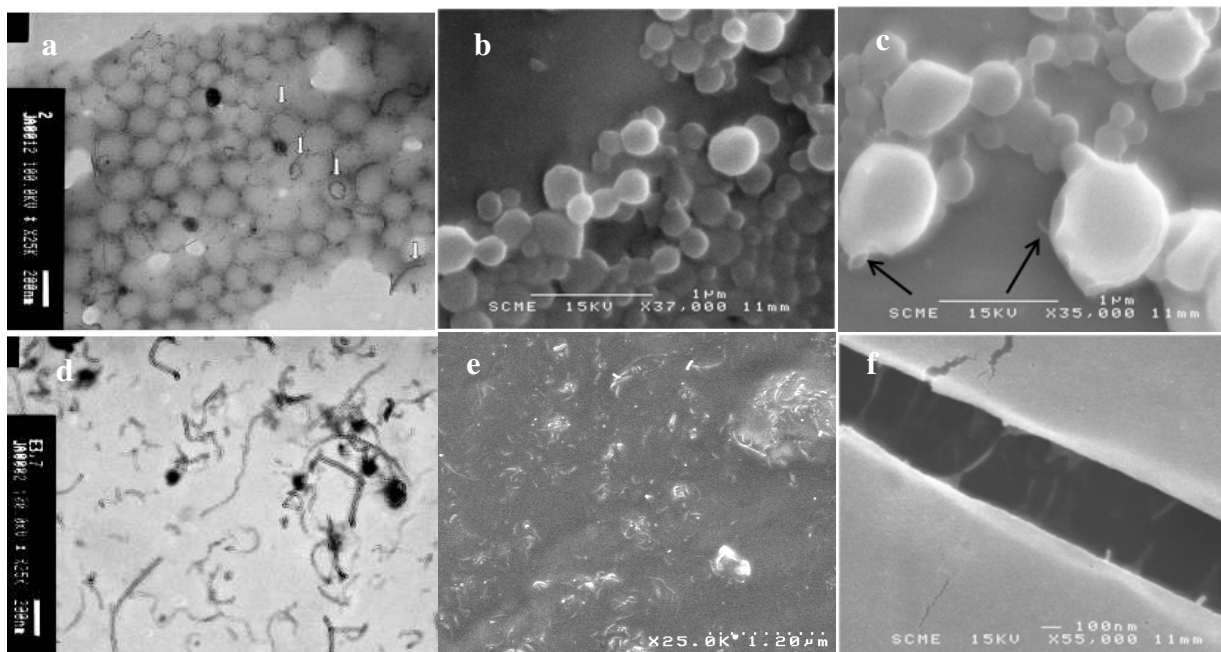


Fig.2. Nanocomposite particles (top) and composite film after annealing (bottom) as observed by TEM (a, d) and SEM (b, c, e, f). Arrow in (a) shows individual CNT entrapped into polymer particles, whereas (b) and (c) shows the non-spherical shapes of the objects due to CNT protruding (showed by black arrows). After annealing, films were composed of long individual nanotubes, visible in the core of the material by TEM (d) or at the surface of the film by SEM (e). A fracture of the film breaks in some extent the CNTs (f). Scales are given vertically and horizontally in TEM and SEM photos.

imposed the initial CNTs/polymer ratio to be applied. Above 5wt%, the yield in dispersion decreases down to 50%, the rest being trapped into non-CNTs containing lumps. Resulting films from samples described in Table 1 were tested on a Pyrolysis Combustion Flow Calorimeter (PCFC)¹⁷ which measures the main heat release characteristics of small samples (1-4mg). It should be noted that PCFC is not sensitive to some physical effects like barrier effect or heat shielding. Since these two effects constitute the main modes of action of CNTs, the reduction in pHRR while incorporating CNTs into a polymer matrix is strongly lower than one would see in cone calorimeter. Still, it is obvious from Table 1 that the peak of heat release rate (pHRR) decreases with CNT contents. This value was found lower than the theoretical value predicted by a linear rule of mixtures (considering that HRR of pure CNT is 0). The temperature of the pHRR increases also (but very slightly) when CNTs are incorporated into the PMMA matrix to stabilize approximately at 2wt% CNTs (compared to polymer). Therefore we could assume that CNTs act not only as diluting filler, but also would trap radicals, indicating a very good dispersion of CNT (the developed interface between the CNT and the PMMA matrix favours radical trapping). Note that similar experiments using a commercial CNT masterbatch obtained by extrusion as starting material did not lead to such improvements (not shown). Such results were confirmed by TGA measurements, with a decomposition curve shifted towards higher temperatures while trapping cholate-stabilized CNTs rather than mixing in the bulk the polymer and CNTs (Figure S6). Such shift was not obvious for CNTs stabilized by NaDBBS, showing the importance of the fine dispersion of CNTs on their thermal efficiency.

Table 1 Influence of the content of CNT on the yield of dispersion and thermal resistance of the nanocomposite films.^a

Initial CNT:PMMA (%)	Final CNT:PMMA (%) ^b	Particle yield (%) ^c	Relative pHRR (%) ^d	pHRR temperature (°C) ^d
0	0	99	100	390
1.0	- ^e	93	88	396
2.3	1.7	78	83	400
4.5	4.2	44	78	403
7.5	- ^e	27	- ^e	- ^e
10	8.9	12	74	401

^a Quantities: 12g of 1wt% PMMA acetone solution and xg of 0.5wt% of aqueous suspension (pH 11, 1wt% surfactant); ^b as given by TGA residue at 500°C (after subtraction of PMMA and surfactant residue); ^c measured after filtration on a paper filter; ^d measured by PCFC (see text for details); ^e not determined.

In conclusion, we have developed a very simple technique to entrap CNTs into a thermoplastic polymer, in a view to generate the finest nanocomposite films. We are currently working on preparing films containing various CNTs contents for measuring electrical conductivities.^{18,†} We also plan to generate nanocomposite particles in sufficient quantities to test such finest composites in a cone calorimeter. This work has been the subject of a patent published recently.¹⁹

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Experimental

Materials and methods:

PMMA (14700g/mol, polydispersity of 1.54) was purchased from Aldrich and used as received. Multiwalls CNTs are Baytubes purchased from Bayer, prepared by CVD with a high degree of purity (low concentration of residual catalyst and absence of free amorphous carbon). Other specifications are: inner mean diameter ~ 4 nm, outer mean diameter ~ 13 nm, typical length ~ 0.2-1 µm after sonification/water dispersion. They were used without further purification. Sodium cholate hydrate (98%) and Sodium dodecylbenzene sulfonate (NaDDBS, 98%) surfactants were provided by Aldrich. NaOH pellets (SDS, 98%), acetone (Analar Normapur), and HPLC grade water (Panreac) were likely used without modification.

The diameter of the CNTs/PMMA nanocomposites was determined by retro-scattered light using a Nanotrak device. Particle size from 8 nm to 6500 nm can be recovered with this apparatus. According to the mass fraction of solvent of the sample, viscosity and refractive index of the dispersing fluid were deduced from tables and used for particle size analysis. The particle morphology was investigated using scanning electron microscopy (SEM). SEM samples were prepared by laying a drop of the dispersion on an aluminium foil and letting the drop air-dried at room temperature. The resulted film consisting of PMMA nanoparticles on aluminium foil was then vacuum-coated with gold and analyzed. Transmission electron microscopy (TEM) was also carried on samples in order to determine the distribution of CNTs in PMMA matrix. A drop of the dispersion was laid on a TEM grid and was left to dry gently at room temperature. Centrifugation of the dispersions was carried out with a Sorvall GLC-2B General Laboratory Centrifuge. Microcalorimetry was carried out on a Pyrolysis Combustion Flow Calorimeter (PCFC) apparatus from Fire Testing Technology Ltd (FTT). The sample was heated under nitrogen stream up to 750°C at a high heating rate (typically 1K/s) from which released gases were evacuated in a combustor, burnt in presence of an excess of oxygen at 900°C. Heat release rate is calculated from oxygen consumption according to the Huggett's relation (1 kg of oxygen corresponds to 13.1 MJ of released energy). Each composition was tested in triplicate. Peak of Heat Released Rate (pHRR) and temperature of the peak of heat release rate (TpHRR) were calculated.

Dispersion of CNTs in water

CNTs and the surfactant were put in water and the resulted solution sonicated under stirring (2 sec power on, 1 sec power off) during one hour with a power of 40%. This first sonication enables to divide big aggregates. The solution was then let to cool during 15 min and sonicated a second time during one hour with a power of 100% in order to divide CNTs bundles. The resulted solution was black and the efficiency of the dispersion could be controlled with an optical microscope. A typical recipe consisted in mixing 0.5g of CNTS, 1g of surfactant and 100g of water. Different fractions of CNTs (issued from the 0.5% CNTs aqueous dispersion) were dropped in a NaOH aqueous solution, set at a final pH 11. Acetone was added drop by drop thanks to a micropipette. After of each addition, dispersion is agitated and pipetted in a capillary. After a rapid visual observation, acetone

was quickly added again and the same procedure carried out. The stability limit placed on the phase diagram was assigned when black dots started to show up throughout the capillary. For larger contents of acetone, big lumps of CNTs aggregates were clearly seen without the need for capillary observation.

CNTs/PMMA nanocomposites formation

The nanoprecipitation consisted in mixing an aqueous phase and an organic phase containing a hydrophilic solvent (Scheme 1). The organic solution was first prepared by dissolving PMMA in acetone. The dispersion of CNTs diluted in the basic solution (water + NaOH) was added quickly to the organic solution under moderate stirring. The solution became grey-black and the dispersion was used as his or after solvent removal by a rotavapor during 15 min at 30°C. A typical recipe consisted in first dissolving 1 g of PMMA in 100 g of acetone to obtain the organic solution. 8 g of the CNTs aqueous dispersion was then poured in 12 g of the organic solution.

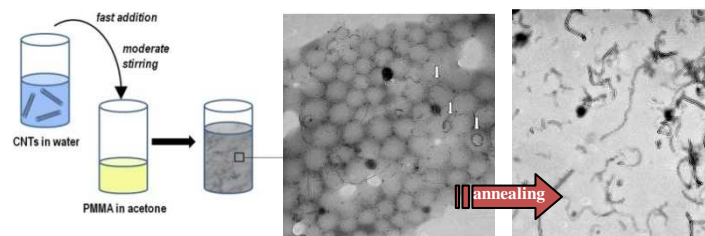
Notes and references

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- ^b Nanoleedge Inc, 75 Bvd de Mortagne suite 121 Boucherville, Québec, J4B 6Y4 Canada.
- ^c Centre de Matériaux de Grande Diffusion, Ecole des Mines d'Alès, 6 Avenue de Clavières 30319 Alès Cedex, France.
- † Electronic Supplementary Information (ESI) available: experimental part, phase diagram for NaDDBS, TEM and SEM photos, TGA curves. See DOI: 10.1039/b000000x/
- ‡ We are facing two difficulties nowadays in the production of nanocomposite films: i) the contents of product that we generally get are very small, since good achievement of Ouzo effect requires high dilutions; ii) the processing of PMMA films, a brittle polymer, is difficult to generate in a standard mold used for electrical measurements, for instance.
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5



Supporting information for

Finest nanocomposite films from carbon nanotubes-loaded poly(methyl methacrylate) nanoparticles obtained by Ouzo effect

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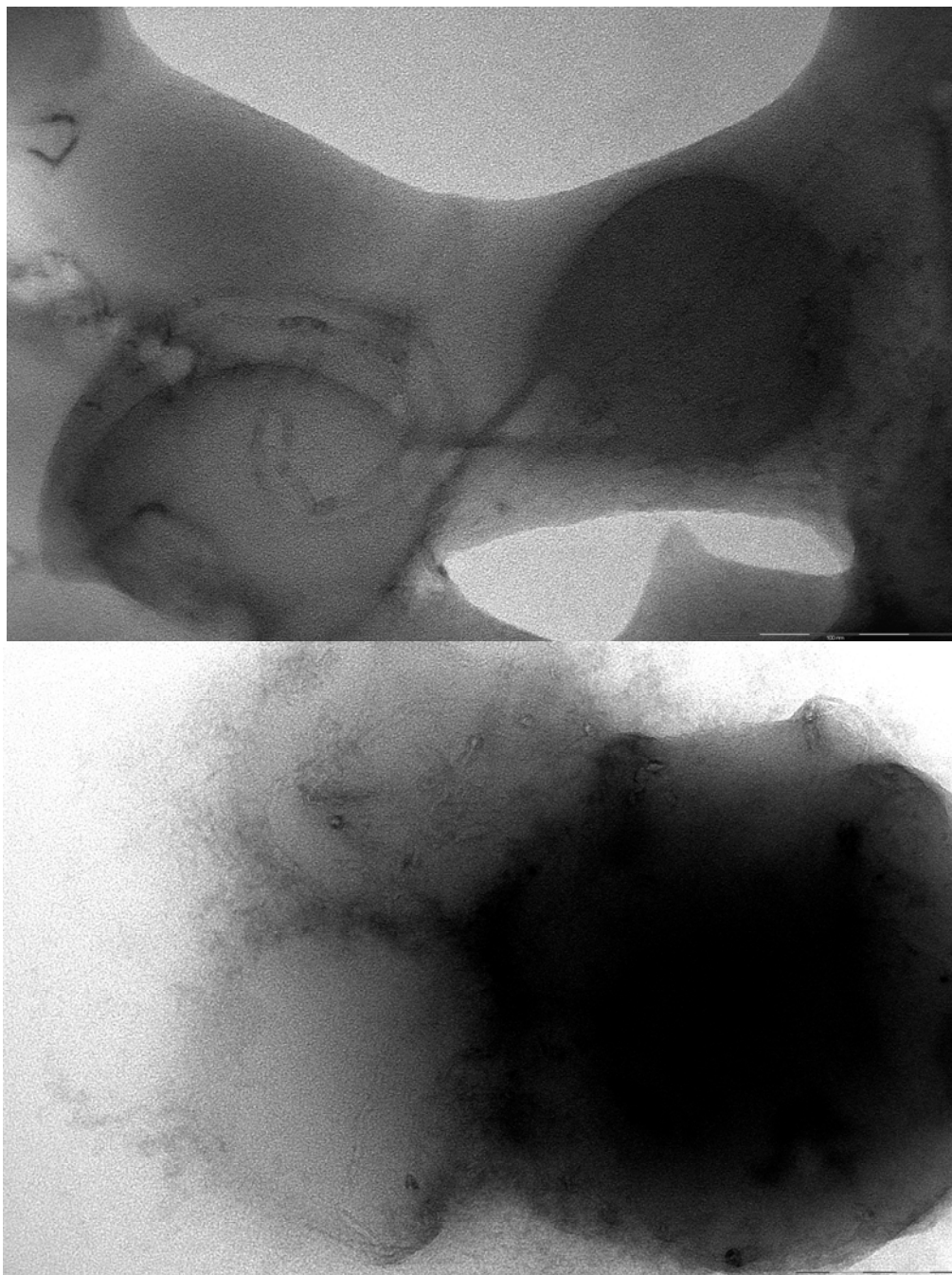


Figure S1: Nanoparticles loaded with few carbon nanotubes in the same particle (typically less than 5). The ratio CNTs:PMMA was set at 1 wt% (top) and 5 wt% (bottom). The scale holds for 200 nm.

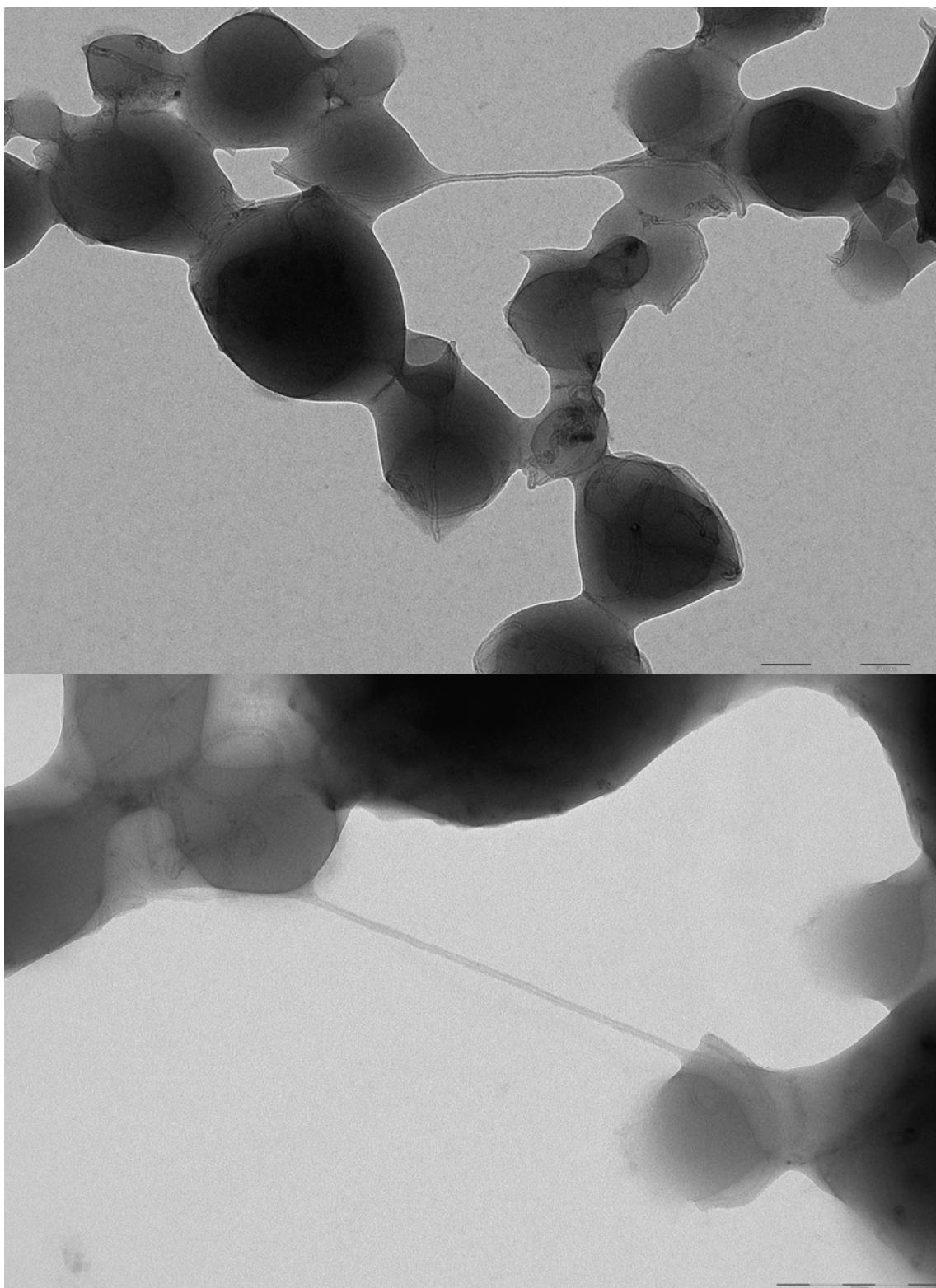


Figure S2: Examples of TEM photos showing long CNTs entrapped within fewer nanoparticles. CNTs:PMMA loading Top: 2wt% CNTs:PMMA loading, bottom: 5wt% (see Table 1 in the main text for details). Scale bar: 200 nm.

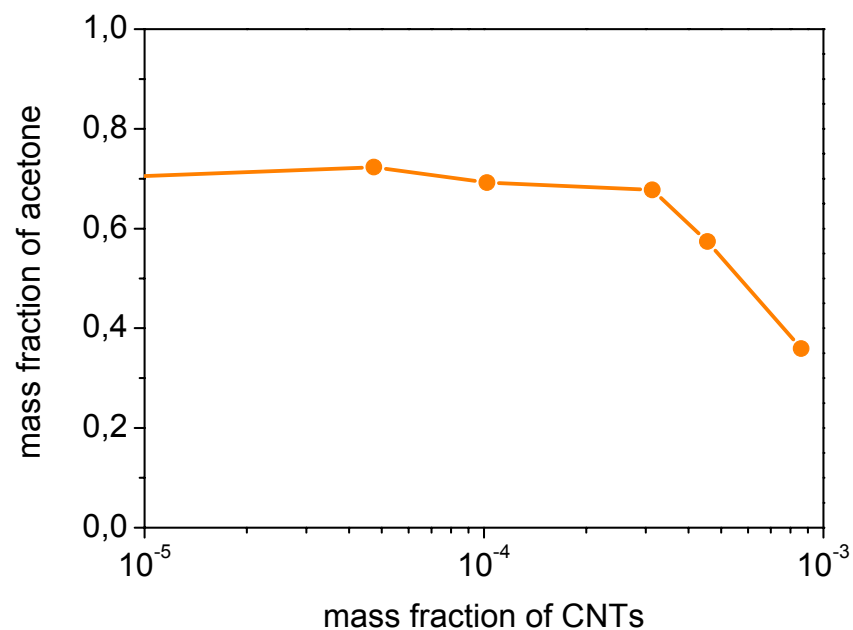


Figure S3: Same plot as Figure 1b in the main text, but with NaDDBS as the surfactant of the CNTs dispersion.

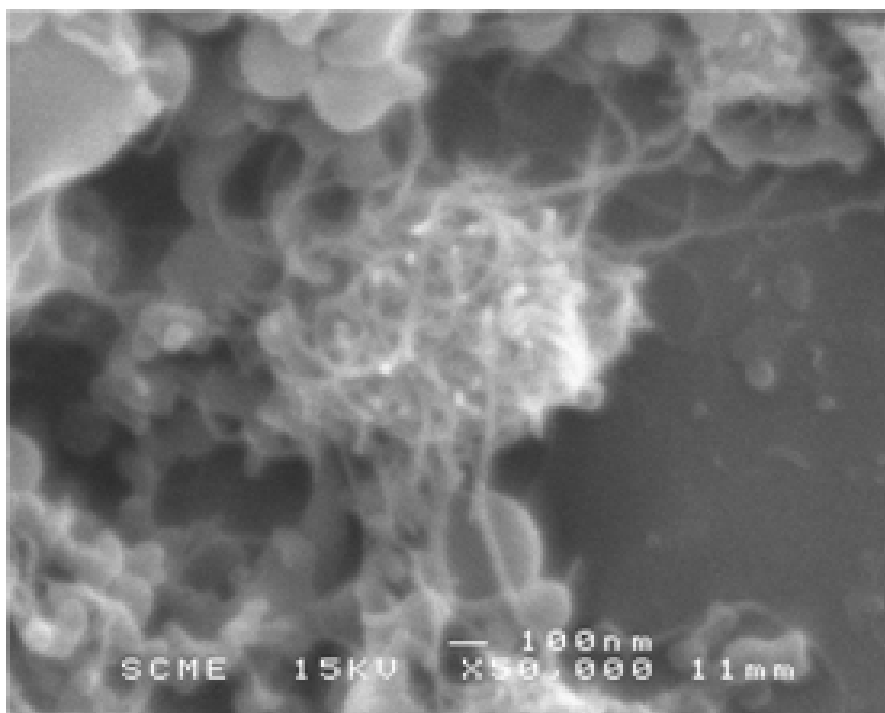


Figure S4: Bundles of nanotubes which were not destroyed while preparing the CNTs dispersion in presence of NaDDBS. These small aggregates were seen in the original dispersion or here after nanoprecipitation (see very small particles on the bottom left handside).

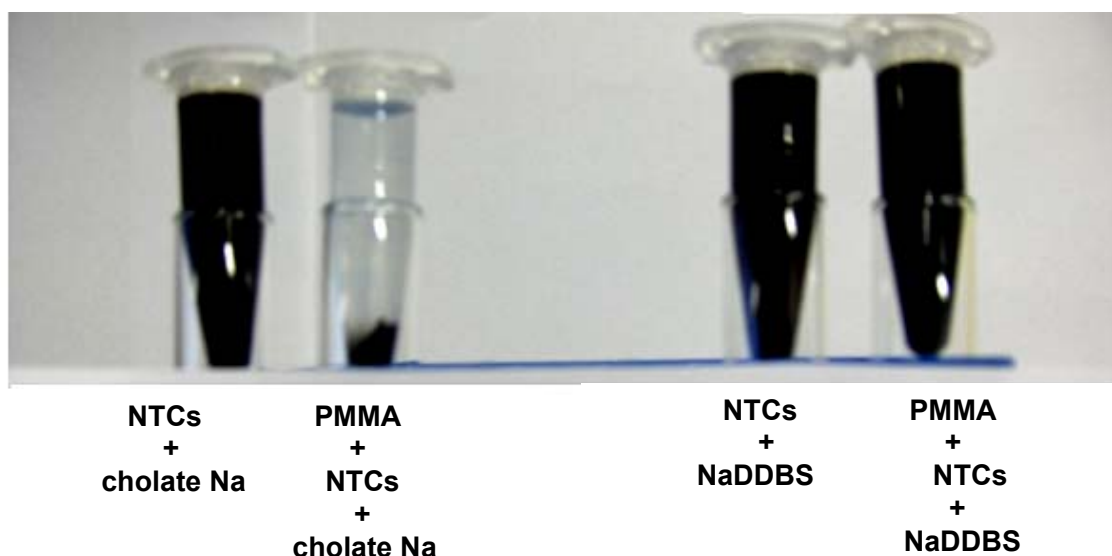


Figure S5: Efficiency of CNTs trapping by PMMA as observed by simple centrifugation experiments. Whereas the cholate sodium based sample was totally entrapped in the particles (on the left), the naDDBS-based sample was in some part still dispersed in the aqueous phase.

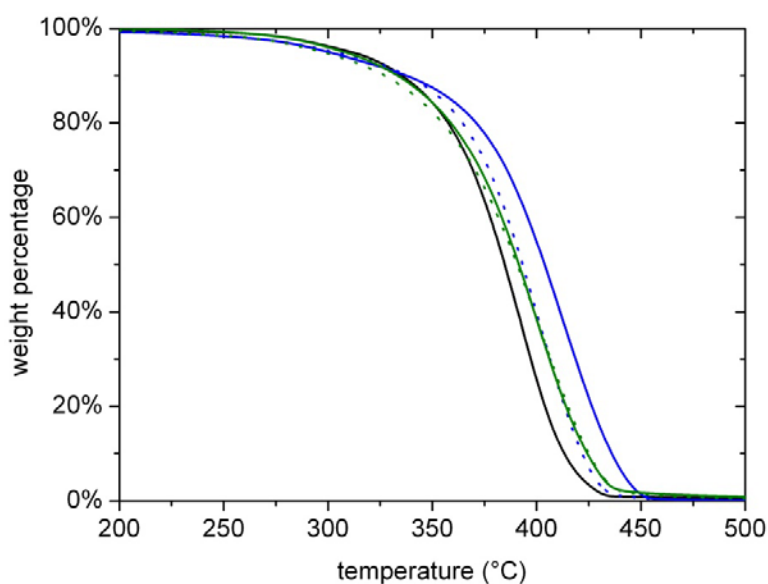


Figure S6. Normalized PMMA decomposition curves obtained by TGA representing PMMA weight percentage versus temperature for PMMA nanoparticles (black line), PMMA-CNT nanocomposites (color solid lines) and for mixtures of PMMA nanoparticles (prepared beforehand by simple PMMA nanoprecipitation) and dispersed CNTs (dotted lines). Sodium cholate based samples are in blue, those stabilized from NaDDBS in green.