

Electronic Supplementary material

The role of polymer-solvent interactions in Polyvinyl- alcohol dispersions of Multi-wall carbon Nanotubes: from coagulant to dispersant

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Equal contribution

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Stable dispersions of MWNTs could not be obtained via sonication in aqueous solutions of PVA. PVA polymers of different molecular weights and degree of hydration were tested (see Table S1).

Table S1: Unsuccessful attempts to disperse MWNTs in aqueous solutions of PVA

#	CNT type	PVA Mw [g/mol]	PVA Concentration [wt%]	CNT Concentration [mg/ml]
1	NTX4	PVA 10-80	1-10	0.5-2
3	NTX4	PVA 23-98	1-5	1
5	INP	PVA 10-80	1-10	0.5-2
6	INP	PVA 85-97	5	1

Stable dispersions of Carbon Black (CB) were obtained by sonication of the dry powder in aqueous solutions of PVA.

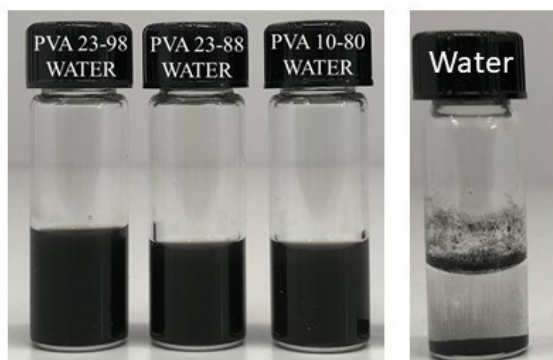


Figure S1. Left: CB (1 mg/ml) dispersions in 5 wt% PVA 23-98, PVA 23-88 and PVA10-80 solutions in water, following 6 weeks incubation. The dispersions were stable for at least 3 months and aggregation was not observed. Right: CB powder (1 mg/ml) in water.

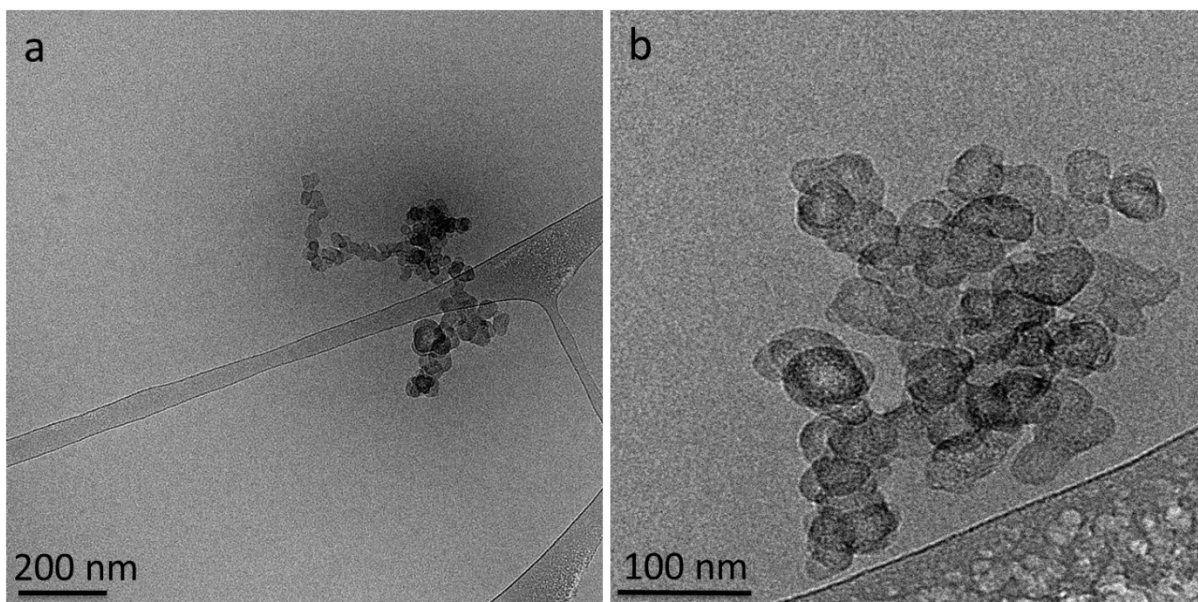


Figure S2. Cryo-TEM of CB (1 mg/ml) dispersion in PVA 10-80 solution in water (5 wt%).



Figure S3. Image of vials containing powders of MWNTs (2 mg/ml) in 50:50 EtOH: water liquid mixtures. Left: immediately after sonication for 120 minutes, following the the protocol described in the experimental part. Right: after a day. Similar images were obtained after centrifugation in 30,000g for 20 minutes.

In figure S3 we present the results of a control experiment: in this experiments powders of MWNTs (NTX4 and INP) were sonicated in a liquid mixture containing 50vol% EtOH but no PVA. The images clearly show that sonication does not lead to the formation of dispersions (left). Furthermore after incubation at ambient conditions of centrifugation the non-dispersed MWNTs settle to the bottom of the vial.

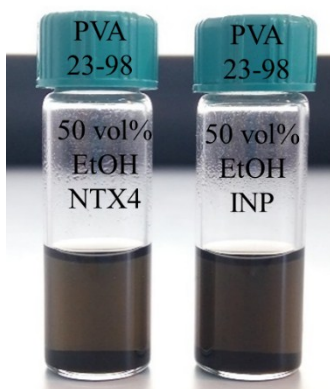


Figure S4. MWNTs-NTX4 (left) and MWNTs-INP (right) powders after prolonged sonication in solutions containing 1%wt PVA with a high degree of hydrolysis (98%), designated PVA 23-98 (see Table 1), in EtOH:water solution (50:50 vol%).

In Figure S4 we present the effect of EtOH on dispersion of MWNTs-NTX4 (left) and MWNTs-
INP (right) in solutions of PVA with a high degree of hydration. Even after prolonged sonication
most of the MWNTs powder is aggregated at the bottom of the vial.

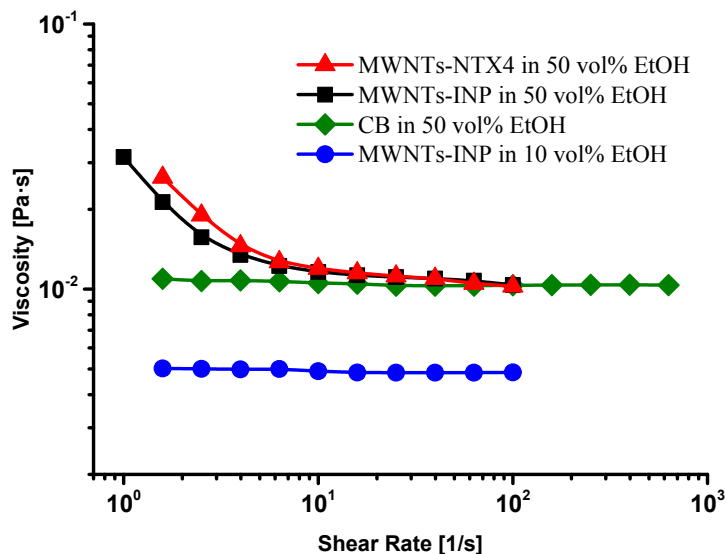


Figure S5. Flow curves of MWNTs and CB dispersions in PVA solutions of 5 wt% PVA10-80 in 50:50 EtOH:water liquid mixtures and (blue) 10:90 EtOH:water liquid mixture.

Thermogravimetric Analysis (TGA).

The experiments were performed using a Mettler Toledo TGA/SDTA851e instrument. 3-17 mg of the sample were placed in an aluminum oxide pan.

Measurements were performed by heating at a constant rate of 20°C min⁻¹ from 40 to 1000°C. The measurements were carried out under a constant flow of nitrogen (200 ml min⁻¹), in an open pan.

A reference measurement was obtained under the same conditions with an empty pan.

To test the decomposition of MWNTs-based samples measurements were carried out by heating at a rate of 20 °C min⁻¹, from 40 to 750 °C maintaining the sample at 750 °C for 9h, and heating at a rate of 20 °C min⁻¹ from 750-1000 °C.

In Figure S6 we present the TGA curves of the different components

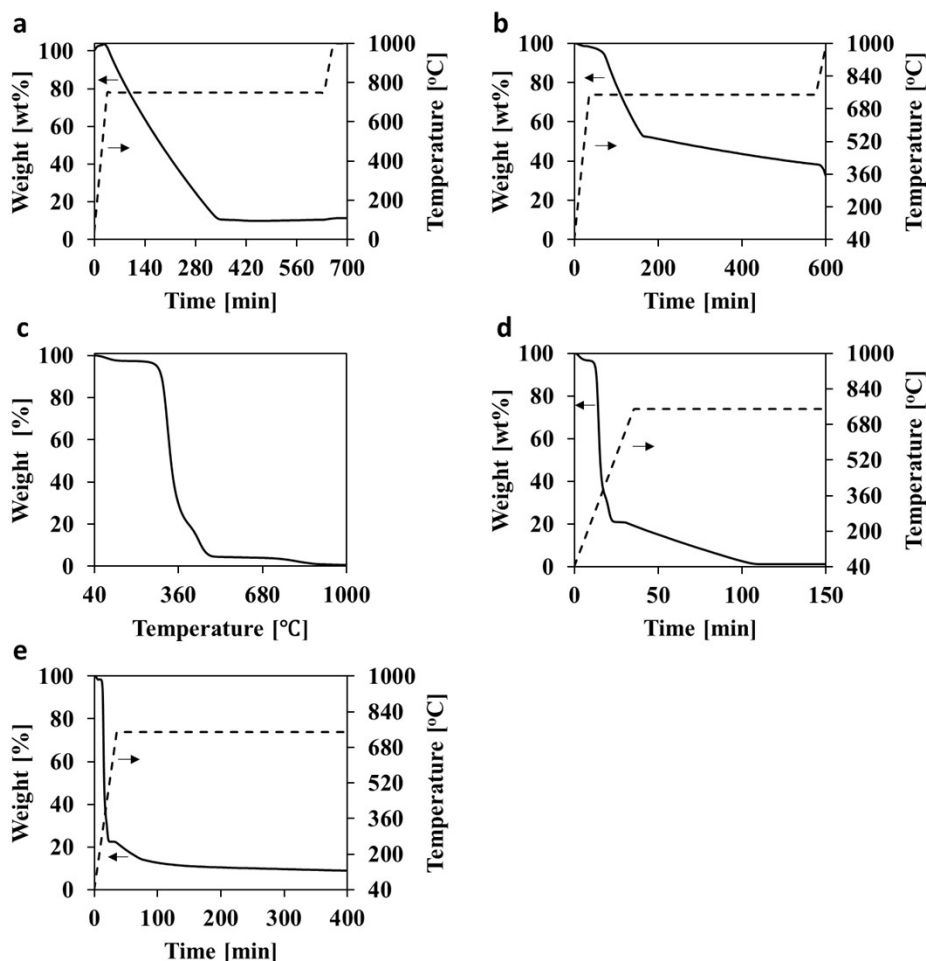


Figure S6. TGA curves of MWNTs powders, PVA10-80 and their mixtures (a) MWNTs-NTX4 (b) MWNTs-INP (c) PVA10-80 and (d, e) mixed powders containing 5:1 mass ratio of PVA10-80:MWNTs-NTX4 and PVA10-80:MWNTs-INP, respectively. Dashed curves outline the temperature profile as a function of time, and the continues line the weight-loss (wt%) as a function of time.

The TGA thermograms of MWNTs-NTX4 and MWNTs-INP powders show a weight loss of 94wt% and 70%, respectively (Figure S6 a, b, respectively) at 750°C (for 9h), according to reported procedure¹. The TGA thermogram of PVA exhibits three main weight losses regions (Figure S6c), as reported before², where the first weight loss at ~90°C is associated with water evaporation, the second weight loss at ~320°C is attributed to the dehydration reaction of the polymer, and the third weight loss above ~ 440°C is attributed to the decomposition of carbonaceous matter.

To calibrate the system we characterized the thermal decomposition of powder mixtures prepared at 5:1 mass ratio of PVA10-80: MWNTs-NTX4 or PVA10-80: MWNTs-INP (Figure S6d, e, respectively).

Similar measurements carried out for characterization of the dried dispersions exhibited similar curves (Figures S7-S8): up to 750°C, three steps of weight loss are observed. The steps are associated with the decomposition of PVA and adsorbed water, while above 750°C, contentious weight loss is attributed to the decomposition of the MWNTs and residues of the polymer. The data is presented in Table S2.

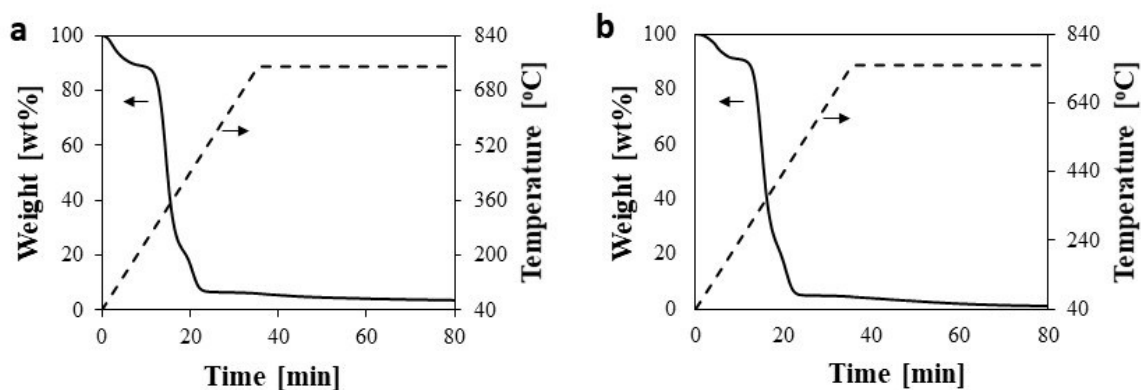


Figure S7. TGA curves of dried dispersions of MWNTs-INP (1 mg/ml) in (a) 1 wt% PVA10-80 in 50 vol% EtOH, (b) 5 wt% PVA10-80 in 50 vol% EtOH. The dashed curves designate weight loss as a function of temperature, and the contentious line weight loss as a function of time.

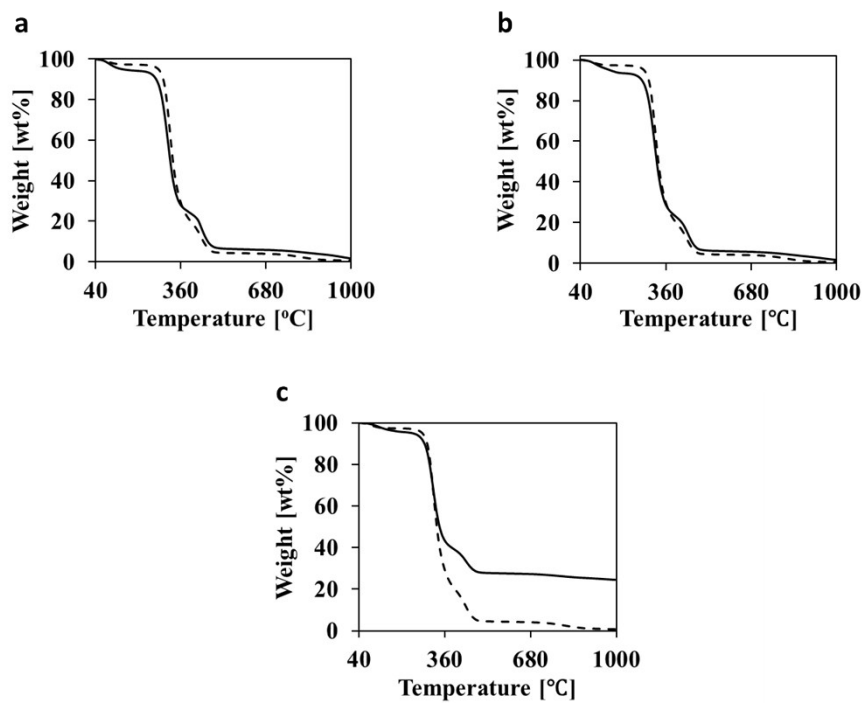


Figure S8. TGA curves of dried dispersions of MWNTs-NTX4 (1 mg/ml) in (a) 1 wt% PVA10-80 in 10 vol% EtOH, (b) 1 wt% PVA10-80 in 50 vol% EtOH, and (c) 5 wt% PVA10-80 in 50 vol% EtOH. The TGA curve of PVA10-80 appears as a dashed curve.

Carbon Black (CB) samples: The thermal decomposition of CB dispersion was investigated. Powder mixtures of PVA/CB were investigated to provide a reference (Figure S9 a). We evaluated the mass fraction of CB in the dispersion by subtracting the weight percent of pure PVA from the dispersion thermogram curve at 750°C (Figure S9b), obtaining the weight percent of the CB in the PVA-CB dispersion, following a procedure outlined in the literature³.

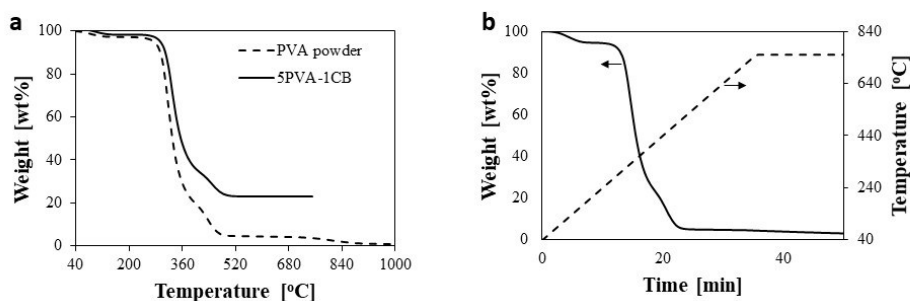


Figure S9. TGA curves of CB (a) a mixture of PVA10-80:CB powders at 5:1 mass ratio (b) dried dispersions of CB (1 mg/ml) in 5wt% PVA10-80 in water. The dashed curves designate weight loss as a function of temperature, and the contentious line weight loss as a function of time.

Table S2: Calculated weight fraction of CNTs and CB in PVA dispersions

Sample description	Weight fraction of NP [wt%]
MWNTs-NTX4, 1wt% PVA10-80, 10 vol% EtOH	1%
MWNTs-NTX4, 1wt%PVA10-80, 50 vol% EtOH	1%
MWNTs-NTX4, 5wt%PVA10-80, 50 vol% EtOH	18%
MWNTs-INP, 1wt%PVA10-80, 50 vol% EtOH	2%

MWNTs-INP, 5wt%PVA10-80, 50 vol% EtOH	4%
CB, 5wt%PVA10-80, water	1%

References

1. Kim J.H.; Lee S.; M.; H.; W.S.; Jeong H.J.; J.R.; J.T.; S.K.; Three-Dimensional Printing of Highly Conductive Carbon Nanotube Microarchitectures. *ACS Nano*, **2016**, 10, 8879–8887.
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