# Influence of different anionic polyelectrolyte dispersants on the rheological and electrokinetic properties of carbon nanotubes

Hamid Sarraf*, Ludmila Škarpová, Petr Louda

Faculty of Mechanical Engineering, Department of Materials, Technical University of Liberec, Halkova 6, 46117, Liberec 1, Czech Republic.

*Correspondence author. E-mail: sarraf_20002000@yahoo.com

ABSTRACT

Rheological (viscosity) and electrokinetic (zeta-potential) properties of multi-walled carbon nanotubes (MWCNTs) with different anionic polyelectrolyte dispersants (polyacrylic acid (PAA), ammonium salt of polymethacrylic acid ($PMAA-NH_4$) and polyaspartic acid (PASPA)) in aqueous systems were investigated. $PMAA-NH_4$ stabilized MWCNT suspensions showed higher maximum solid loading and lower intrinsic viscosity than other polyelectrolytes stabilized MWCNT suspensions.

## INTRODUCTION

The solubility and the dispersion of MWCNTs gave limitations for real processing for CNT hybrid materials. To enhance these properties of MWCNTs, some approaches were suggested, such as, surfactant mixing, chemical oxidation, and polymer coverage distribution (wrapping) on the particle surface[1,2]. Especially, polymer surface coverage distribution using polyelectrolytes was suggested as efficient approach to disperse MWCNTs in solutions. The interesting feature of polyelectrolyte dispersants is that they maintain the stability of slurries by electrostatic, steric and electrosteric forces. In this study three different anionic polyelectrolyte dispersants have been used. Polyacrylic acid (PAA) which has been widely used as polyelectrolyte dispersant for ceramic processing, such as, paint, adhesive, and paper industry. Polyaspartic acid (PASPA), an amino acid polymer which has been investigated for replacing PAA in environmental friendly applications because PASPA is biodegradable. And finally, an alkali-free anionic polyelectrolyte (Dolapix CE64) dispersant which is delivered as a 70 wt% aqueous solution and contained 30 wt% of the ammonium salt of poly-methacrylic acid ($PMAA-NH_4$) that imparts stability by electrosteric interactions with a pH of 9. It had a mean molecular weight of 350 g/mol[3]. In this study, dispersant concentration is expressed in weight % on dry powder basis.

Though chemical reactions between polyelectrolytes and CNTs were investigated[4,5], there were few studies on the electrokinetic and rheological behaviors of CNTs with polyelectrolyte dispersants. This paper reports the electrokinetic and rheological properties of MWCNT slurries with PAA, PASPA and $PMAA-NH_4$ (Dolapix CE64). Zeta potential and rheological (maximum solid loading and intrinsic viscosity) properties of MWCNT slurries with PAA, PASPA and $PMAA-NH_4$ were investigated.

## EXPERIMENTAL

Commercially available MWCNTs (Iljin Nanotech. Inc., CVD method, 95%) were used in this study. A commercial ammonium salt of polymethylacrylic acid (Dolapix

CE64, PMAA-$NH_4$) as alkali-free anionic polyelectrolyte dispersant was purchased from Zschimmer & Schwarz GmbH Co. (Germany). Polyaspartic acid (PASPA) was obtained from Bayer Corp. All following materials were obtained from Aldrich Chemical Co. and used as received: Polyacrylic acid (PAA), potassium hydroxide (KOH, 1 M), hydrochloric acid (HCl, 1 M), sodium chloride (NaCl, 99%). MWCNT raw soot was heated in air at 450 °C for 2 h, and then soaked in hydrochloric acid for 24 h and centrifuged. The precipitate was rinsed with de-ionized water three times and dried. To evaluate the surface activity of polyelectrolyte dispersants in MWCNTs aqueous suspensions, electrokinetic (Zeta- potential, pHiep, pH) measurements were carried out with an advanced electrokinetic sonic amplitude (ESA) technique (Device ESA-8000, Matec Applied Science, USA) in this study. This technique is able to determine simultaneously the zeta potential, pH, electrophoretic mobility and isoelectric point of suspensions at a nominal frequency of 1 MHz. Separate measured amounts of MWCNTs, deionized water, sodium chloride ($10^{-5}$ M) and polyelectrolyte dispersants were ultrasonicated with a high-energy ultrasonic horn for 30 min and then equilibrated for 10 min to assure equilibrium adsorption. The pH of the MWCNTs slurry was adjusted to 9.0 by adding 1 M potassium hydroxide. This procedure was repeated for slurries with all solid loadings.

The viscosity variation was measured at 23°C using a concentric cylinder rheometer (Sensor Z41, RV1, Thermo Haake, Ltd., Germany), which is able to measure the corresponding viscosity and shear stress under controlling shear rate. The slurry was pre-sheared at 1000 $s^{-1}$ for 1 min, then, kept stationary for 1 min to equilibrate and then, the shear rate was ramped from 0.003 to 1000 $s^{-1}$. The relative viscosity ($\eta_r$) was calculated as a ratio of the viscosity of the MWCNT suspension ($\eta$) to the viscosity of deionized water ($\eta_0$) at the same temperature.

RESULTS AND DISCUSSION

Fig. 1a shows the FE-SEM image of MWCNTs. The diameter of MWCNT ranged from 10 to 30 nm. The length of MWCNT ranged from 2 to 5 µm, after precipitation and drying process.

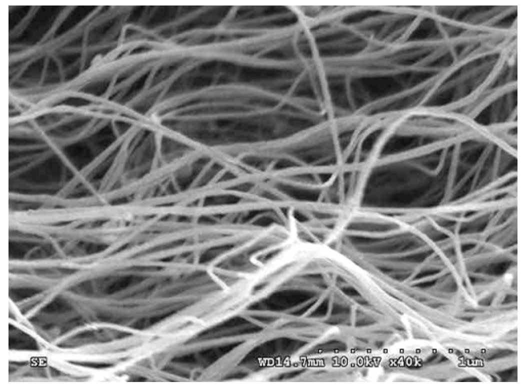


Figure 1. The SEM image of MWCNTs.

<u>Zeta potential measurement</u>

The zeta potential of MWCNTs with polyelectrolyte dispersants as a function of pH is shown in Fig. 2.

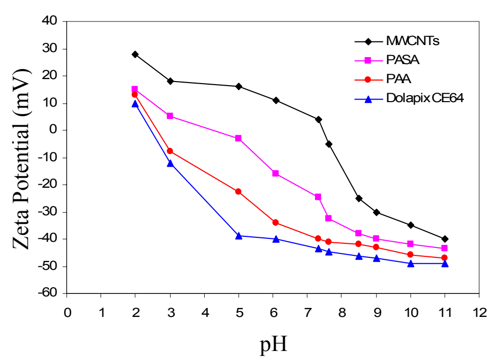


Figure 2. Zeta potential of MWCNT slurries as a function of pH with 0.07 wt.% polyelectrolyte dispersants (raw MWCNT (♦), PASPA (■), PAA (●) and PMAA-NH4 (Dolapix CE64,▲)).

The isoelectric point of the MWCNT was measured around pH 7.6. It was found that the addition of polyelectrolytes made the isoelectric points of MWCNT suspensions shift to lower pH ranges. The addition of 0.07 wt.% (against the total weight of samples) PAA, PASPA and PMAA-$NH_4$ (Dolapix CE64) shifts the isoelectric point of MWCNT suspensions to pH ~ 2.7, ~ 4.2 and ~ 2.4, respectively.

<u>Rheological measurements</u>

The shear thinning behavior was observed with 2 vol% MWCNT suspensions (0.07 wt.% dispersants) as shown in Fig. 3a. The viscosity of MWCNT suspensions decreased sharply at very low shear rate. Fig. 3b shows the optimum amount of dispersants.

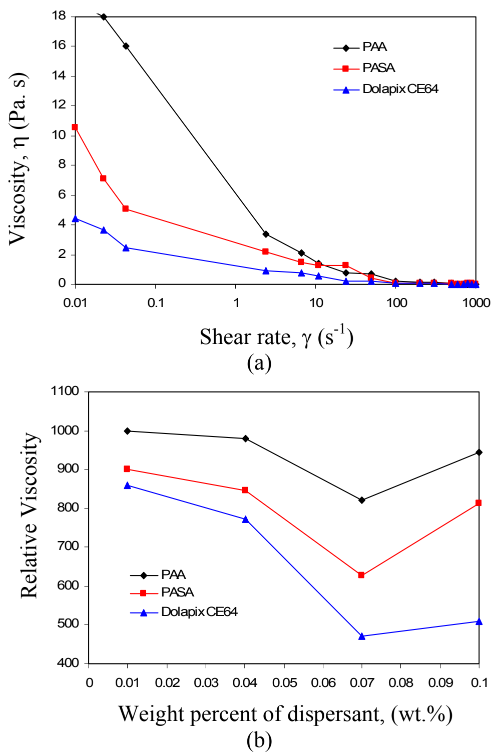


Figure 3. Viscosity variation with changing shear rate at 2 vol% MWCNT slurries with 0.07 wt.% dispersants (PAA (♦), PASPA (■) and PMAA-$NH_4$ (▲)) (a) and the relative viscosity variation with changing the amount of dispersants at 2 vol% MWCNT slurries (PAA (♦), PASPA (■) and PMAA-$NH_4$ (▲)) at 50 $s^{-1}$ (b).

The optimum amounts of PAA, PASPA and PMAA-$NH_4$ were observed around 0.07 wt.%. The relative viscosity of MWCNT suspension increased sharply with less and more added dispersants than the optimum amount of the dispersant. Fig. 4 shows the relative viscosity of MWCNT suspensions as a function of the solid loadings (0.05, 0.5, 2.5, 5 and 7.8 vol.%) with different dispersants. The amount of dispersant was 0.07 wt.%.

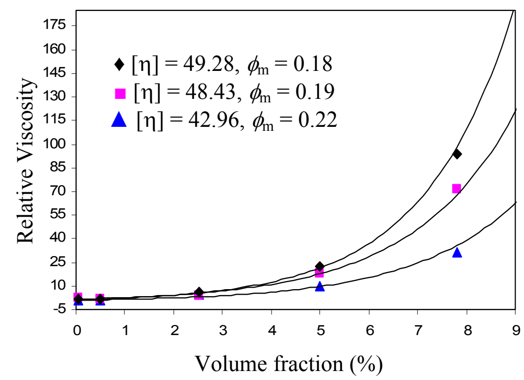


Figure 4. Relative viscosity variation with changing solid loading (0.05, 0.5, 2.5, 5, 7.8 vol.%) at 0.07 wt.% dispersants (PAA (♦), PASA (■) and PMAA-$NH_4$ (▲) at 100 $s^{-1}$. Results were fitted into Krieger–Dougherty equation.

As it can be seen from Fig. 4, the maximum solid loading (fitted by Krieger–Dougherty equation)[6] of PMAA-$NH_4$ (Dolapix CE64) stabilized MWCNT slurry ($\phi_m = 0.22$) is higher than that of PASPA stabilized MWCNT slurry ($\phi_m = 0.19$) and PAA stabilized MWCNT slurry ($\phi_m = 0.18$) which were used as dispersants. Simultaneously, intrinsic viscosity of the PMAA-$NH_4$ stabilized MWCNT slurry ($[\eta] = 42.96$) is lower than both of the PAA stabilized MWCNT slurry ($[\eta] = 49.28$) and the PASA stabilized MWCNT slurry ($[\eta] = 48.43$).

It is suggested that slightly higher maximum loading (which is calculated based on Krieger–Dougherty equation)[6] of PMAA-$NH_4$ stabilized MWCNT slurry may be caused by more efficient polymer wrapping around MWCNTs to enhance the stability of MWCNT slurries and also due to its electrosteric fucntion.

## CONCLUSION

The electrokinetic (zeta potential) variation and rheological (viscosity and maximum solid loading) behavior of MWCNT slurries with different anionic polyelectrolyte dispersants were investigated. Dolapix CE64 ($PMAA-NH_4$) stabilized MWCNT slurries showed higher maximum solid loading and lower intrinsic viscosity than PASPA and PAA stabilized MWCNT slurries. These enhanced properties of Dolapix CE64 stabilized slurries may be caused by the enhanced polymer wrapping from the chemical structure of Dolapix CE64 due to its electrosterical function.

## ACKNOWLEDGMENTS

The financial support from the Technical University of Liberec (TUL) under research grant (MSM 4674788501) obtained from Ministry of Education, Youth and Sports of the Czech Republic is gratefully acknowledged.

## REFERENCES

1. Fu, K.F. and Sun, Y.P., *J. Nanosci. Nanotechnol.* 3 (2003), p. 351.

2. Sun, Y.P., Fu, K.F., Lin, Y. and Huang, W.J., *Acc. Chem. Res.* 35 (2002), p. 1096.

3. Dakskobler, A. and Kosmac-breve, T., "Weakly Flocculated Aqueous Alumina Suspensions Prepared by the Addition of Mg (II) Ions", J. Am. Ceram. Soc., 83 [3] 666–68 (2000).

4. Kim, B.,Park, H. and Sigmund, W.M., *Langmuir* 19 (2003), p. 2525.

5. Artyukhin, A.B., Bakajin, O., Stroeve P., and Noy A., *Langmuir* 20 (2004), p. 1442.

6. I. M. Krieger and T. J. Dougherty, *Trans.Soc. Rheol.,* 3, 137-152, 1959.