Colloids and Surfaces A: Physicochem. Eng. Aspects 489 (2016) 57–66

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Influence of the wetting behavior and surface energy on the dispersibility of multi-wall carbon nanotubes

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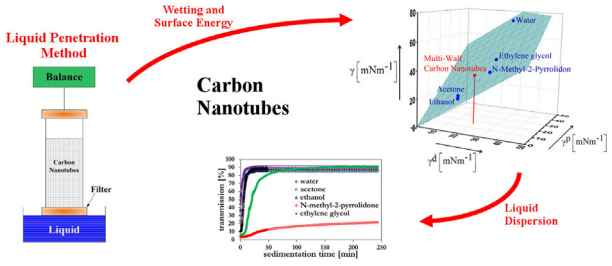
HIGHLIGHTS

- The wetting behavior of carbon nanotubes was studied with liquid penetration method.
- The surface energy with disperse and polar fraction were derived.
- Carbon nanotubes exhibited a significant disperse and polar component.
- Good dispersibility in fluids with similar disperse and polar surface energies.
- Evidence of the influence of particle interactions by covalent functionalization.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 July 2015
Received in revised form 9 October 2015
Accepted 17 October 2015
Available online 23 October 2015

Keywords:
Carbon nanotubes
Functionalization
Wetting behavior
Surface energy
Dispersion

ABSTRACT

Carbon nanotubes (CNTs) possess extraordinary particle properties which make them ideal for the development of innovative polymer composite materials. Because of the tendential agglomerate forming of CNTs, their homogenous exfoliation in organic or inorganic phases is often required and can be obtained by mechanical stressing of the agglomerates. However, the CNT-exfoliation is only achievable in few fluids. Therefore, the CNT-functionalization which means the covalent attachment and modification of the particle surface with functional groups or molecules is applied to alter particle interactions and in this way, their dispersing behavior. The poor CNT-dispersibility in fluids and CNT-dispersion strategies as the functionalization show the importance of the characterization of their particle interactions.

In order to describe CNT/fluid-interactions the wetting behavior was characterized by contact angle measurements with the capillary liquid penetration method. The CNT-surface energies regarding Owens and Wendt could be estimated from the measured contact angles. Thereby, non-modified CNTs exhibited a good interaction with molecules of longer alkyls and even polar liquids and showed further a significant dispersive and polar fraction of the surface energy. The determined surface energies were used for the explanation and estimation of the CNT-dispersibility in liquids. Successful dispersions could be achieved with fluids of similar dispersive and polar fractions compared with those of the particles. Furthermore, ethylamine-functionalized CNTs possessed an enhanced polar component of their surface energy which demonstrated that the CNT/fluid-interactions can be controlled by covalent CNT-functionalization.

1. Introduction

Carbon nanotubes (CNTs) are tubular carbon particles with shells of one or more graphite layers distinguished as single-wall (SWNT) and multi-wall (MWNT) [1]. These particles possess extraordinary properties as a high aspect ratio [2], enormous

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http://dx.doi.org/10.1016/j.colsurfa.2015.10.027
0927-7757/

Table 1
Surface energy characterization of non-functionalized carbon nanotubes given in literature.

Method for the contact angle characterization	CNTs	Model	γ_{sv}	γ_{sv}^{d} [mN m^{-1}]	γ_{sv}^{p} [mN m^{-1}]	Refs.
AFM-method	MWN T	OWRK	27.8	17.6	10.2	[19]
SEM-images of polymer droplets on CNTs (nano-composites)	MWN T	OWRK	45.3	18.4	26.9	[20]
Sessile drop method on CNT-cushions	MWN T	OWRK	82.6	4.8	77.8	[18]
TEM-images of melted metal droplets on CNTs	SWN T	Zisman	40–80			[21]

Table 2
Carbon nanotube-materials and specification.

CNT-material	Carbon purity[a]	Functionalization
MWNT^{p} (Baytubes® C150P)	>95%	None
MWNT^{hp} (Baytubes® C150HP)	>99%	None
MWNT-ethylamine	Not specified	Ethylamine<1% *N*, 1.8% O (elementary analysis)[a] 0.1 at % N, 0.9 at % O(XPS)[a]

[a] Data and characterization of the CNT-materials from the producer and/or project partner BASF.

Table 3
Properties of wetting and dispersing fluids.

Fluid	ρ_l [gcm^{-3}]	η_l [mPas]	γ_{lv} [mN m^{-1}]	γ_{lv}^{d} [mN m^{-1}]	γ_{lv}^{p} [mN m^{-1}]	Refs.
n-Hexane	0.661	0.326	18.4	18.4	0	[a]
n-Heptane	0.684	0.409	20.4	20.4	0	[a]
n-Octane	0.703	0.542	21.8	21.8	0	[a]
n-Decane	0.73	0.929	23.9	23.9	0	[39]
n-Dodecane	0.749	1.35	25.4	25.4	0	[39]
n-Hexadecane	0.773	3.34	27.6	27.6	0	[39]
Methanol	0.792	0.577	22.7	16	6.7	[a]
Ethanol	0.789	1.162	22.1	17.5	4.6	[a]
1-Butanol	0.81	2.544	24.93	[c]	[c]	[a]
1-Hexanol	0.814	4.578	25.81	[c]	[c]	[a]
1-Octanol	0.827	9.12	27.6	21.3	6.3	[40]
Ethylene glycol	1.11	21.81	48	29	19	[a]
Polydimethylsiloxane	0.9	2.79	19.4	19.4	0	[a,b]
Acetone	0.79	0.322	23.3	16.5	6.8	
Acetonitrile	0.78	0.316	28.66	[c]	[c]	
Dimethyl sulfoxide	0.5	0.5	44	36	8	[a]
N-Methyl-2-pyrrolidone	1.023	1.68	40.79	29.21	11.58	[a]
Dimethylformamide	0.949	0.899	37.1	29	8.1	[a]
Diiodomethane	3.325	2.762	50.8	50.8	0	[39]
Water	0.998	1.002	72.8	26	46.8	[39]

[a] Database Tensiometer K100, Krüss GmbH.
[b] Specification sheet 19.05.2011, 4106 Silikonöl M3, Carl Roth.
[c] Unknown.

mechanical strength [3], electrical [4] and thermal conductivity [5] combined with low material densities [6]. These properties make carbon nanotubes very attractive for use in the development of innovative materials in a variety of fields [2,7]. However, the design of CNT-applications is challenging since carbon nanotubes strongly agglomerate and form bundles, that means the parallel alignment of individual CNTs, driven by Van-der-Waals attraction and their huge aspect ratios [8,9]. Therefore, the application of CNTs in innovative developments often requires their dispersion in organic or inorganic fluids which can be achieved by the mechanical stressing of the agglomerates [10]. The ultrasound dispersion is thereby frequently applied [8–11]. However, the carbon nanotube exfoliation is only possible in few liquids whereby the CNT-dispersion is often enhanced by physical or chemical functionalization. Physical functionalization denotes the adsorption of amphiphilic molecules or macromolecules [12] while the chemical modification is the covalent bonding of functional groups or molecules [13] onto the CNT-surface. With these methods interparticle and particle/fluid-interactions are aimed to be altered [10].

The different CNT-dispersion strategies display the importance of the characterization of particle/fluid-interactions of CNTs concluding changes by functionalization techniques regarding the CNT-dispersibility. In literature, for example, Ham et al. [14] compared the dispersion of SWNTs in different liquids and aqueous surfactant systems with fluid parameters. They offered a strong influence of the dispersive component of Hansen solubility parameters [15] whereas high polar and hydrogen bonds could be neglected. In contrast, Bergin et al. [16] estimated Hansen parameters of $<\delta_D> = 17.8\ MPa^{1/2}$, $<\delta_P> = 7.5\ MPa^{1/2}$ and $<\delta_H> = 7.6\ MPa^{1/2}$ for solvents with good dispersibility properties for SWNTs. However, they concluded that the full understanding of the fluid dispersibility of carbon nanotubes remains to be understood [16].

The science of wetting provides suitable models for the explanation of CNT/fluid-interactions since it characterizes the interaction behavior of fluids on solid surfaces. In literature, the CNT-wetting is frequently investigated through contact angles measurements on CNT-buckypapers or cushions by the sessile drop method [17,18]. Sobolkina et al. [17] determined water contact angles on buckypapers of different types of carbon nanotubes. However, they mentioned that the contact angle can only be roughly quantified due to the surface roughness. A precise method for the characterization of the wetting of one individual CNT could be derived from atomic force microscopy (AFM) [19]. On that microscopic scale also transmission and scanning electron microscopy (TEM and SEM respectively) were applied to contact angle estimations of melted metal or polymer droplets on carbon nanotubes [20,21]. Besides, a powder immersion test showed that CNTs can be generally wetted with liquids of surface tensions lower than 200 mNm^{-1} [21–23] which can even fill the inner side of open tubes by their capillarity [24,25]. Kakade and Pillai [26] investigated the wetting behavior