# ADVANCED STUDY OF MULTIWALL NANOTUBE SURFACE TENSION AND CONTACT ANGLE

**S. A. Filatov, O. S. Filatova, E. A. Bykova, P. N. Kumeisha, G. S. Kuchinsky**
Hydrogen Power Laboratory
Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus,
P. Brovka, 15, Minsk, 220072, Belarus
Tel. +375-17-2842238; fil@hmti.ac.by

**Abstract**

The contact angle between multiwall carbon nanotubes and metals was measured by scan electron microscopy. It was shown that specific surface energy parameters for carbon nanomaterials (CNM) can be measured. Direct method (by electron microscopy) and indirect method (by measuring of contact angle of bidistilled water on CNM coating) were tested.

**KEYWORDS**
Carbon nanotubes, surface tension, contact angle, tensiometry, goniometry.

Carbon nanotubes (CNT) based composites play an important role in novel technologies [1–5]. Unique strength and stiffness of reinforced polymer composites on carbon fibers base is well known. Mechanism of interaction between CNT and liquid (polymers, light metals) play key role in understanding of physical performance of the composite, its corrosion and moisture resistance, wet ability. Wetting of nanotubes by the surrounding media is necessary in order to couple the inherent strength of the nanotubes to the matrix, unless direct chemical bonding is induced [6].

The precise characterization of the engineered materials of surface properties is important for the development of new materials for microscale heat pipes and microscale heat exchangers. The knowledge of raw materials surface properties has become a key aspect for this application. Measurement of contact angles and surface tensions provides better understanding of the interactions between solids and liquids (Fig. 1). These interactions also play a key role in understanding of adhesion, material wettability, biocompatibility, lubricity of solid surfaces as well as wetting, washability, spreading and adsorption of liquids. Contact angle and surface tension measurements provide the information needed for development and modification of liquids and solid surfaces using today's sophisticated surface engineering techniques. Due to the unbalance of forces at the surface/interface (Fig. 1) the structure and composition of the surface/interface are different than in the bulk. Interactions at surfaces/interfaces therefore result in special orientations of molecules, accumulation of certain types of molecules at the interface, separation of positive and negative charges. This often may provide a situation when the surface/interface properties are completely different from the properties of the bulk material.

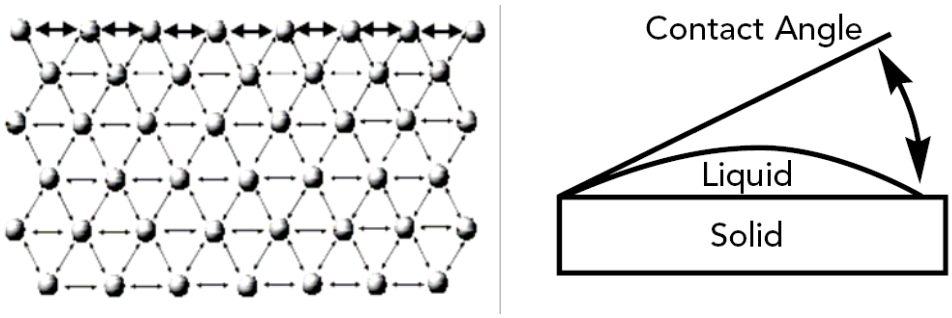
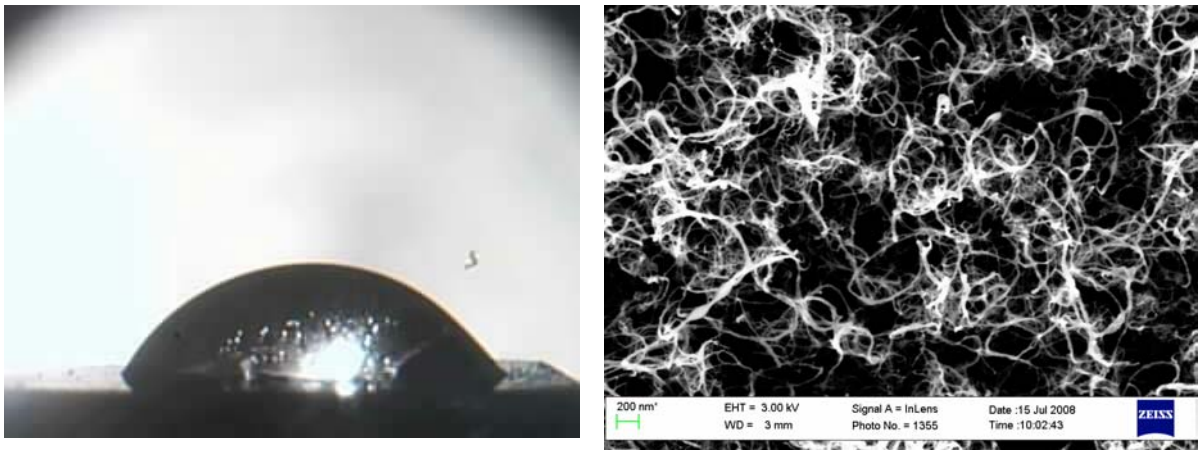



Fig. 1. Typical unbalance of interactions at the air (top) to liquid (down) interaction and contact angle description

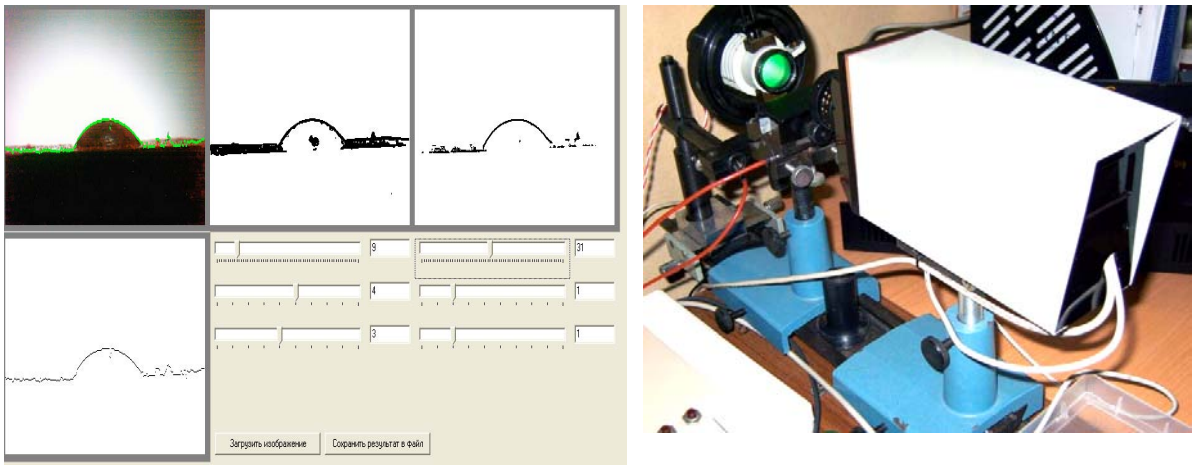
A useful measurement of the ability of liquid to wet surface is known as contact angle. Contact angle is the angle between the solid surface and the tangent to the liquid surface at the place of contact. If the contact angle is greater than 90 degrees, the liquid tends to bead up. Liquids having contact angles less than 90 degrees tend to wet surfaces. A contact angle of 0 degrees indicates a liquid will completely cover a surface, while a contact angle of 180 degrees indicates the liquid beads up on a surface. Measurement procedure required a precise volume droplet of pure water placed on the film surface, fig. 2.




*a)* *b)*

Fig. 2. Water micro droplet on CNT coating (*a*) and electron image of CNT coating (*b*)

Physical methods of measuring contact angles and surface tensions based on tensiometry and goniometry are very useful techniques for surface and liquid characterizations due to their universality, high accuracy and simplicity. On Fig. 3 our experimental setup for automatic contact angle measurements is shown.




*a)* *b)*

Fig. 3. Experimental setup on high resolution camera base (*a*)
and screen shot of software for automatic contact angle measuring (*b*)

For indirect measurement of surface tension CNT coating on we need to obtain image of drop by camera and make automatic measurement of contact angle by our own software, fig. 4.

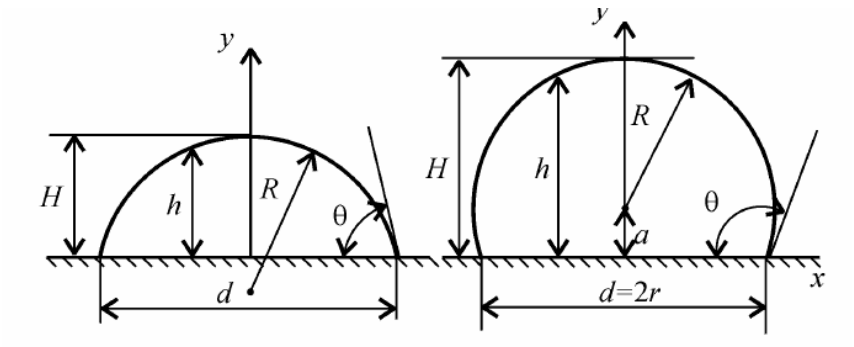



Fig. 4. Model of liquid drop on solid surface

By automatic procedure *H* and *d* parameters of drop are measured and contact angle are calculated by equation

$$\theta = 2arctg\frac{2H}{d} = \arccos\left(1-\frac{H}{R}\right) = \begin{cases} \arcsin\dfrac{d}{2R}, & \theta < 90^0, \\ 180^0 - \arcsin\dfrac{d}{2R}, & \theta > 90^0. \end{cases} \quad (1)$$

On the other hand

$$\cos\theta = \frac{\sigma_u - \sigma_{ul} - R\dfrac{d\sigma_l}{dR} - \dfrac{r}{2}\dfrac{d\sigma_{ul}}{dr}}{\sigma_l + R\dfrac{d\sigma_l}{dR}}, \quad (2)$$

where surface energy can be expressed by Tolman equation as follows:

$$\sigma_l = \sigma_l^{\infty}(1-\alpha C). \quad (3)$$

However, these tensiometry and goniometry measurements are the only techniques for getting of the properties of the outermost layer of the surface/interface, but simultaneously they are fast, simple and accurate techniques for quick evaluation e.g. of surface treatments of solids or liquid formulations. Image information tools such as transmission and scanning electron microscopy (TEM and SEM) give possibility for direct measurements of “wet” ability of CNT.

In our experiments we use multiwall CNT manufactured in laboratory by CVD technology by thermal cracking of isobutene, as carbon carrier. Drops on CNT surface were obtained by special laser ablation technique, fig. 5, and were investigated by Zeiss Supra 55 SEM microscopy unit and Thermo Nicolet Raman spectrometer.

By direct measuring of drop parameters and equation from [6] it is possible to obtain next equation:

$$\frac{\nu_l(1+\cos\theta)}{2\sqrt{\nu_l^D}} = \sqrt{\nu_s^P}\left(\frac{\sqrt{\nu_l^P}}{\sqrt{\nu_l^D}}\right) + \sqrt{\nu_s^D}, \quad (4)$$

that gives capability for calculation of polar and dispersive components of the solid surface free energy, $\nu_s^P$ and $\nu_s^D$ respectively.

By means of this unique and simple technology a possibility of investigation of surface energy of CNT coatings and CNT surface energy for different types of carbon nanotubes and carbon fibers is available.

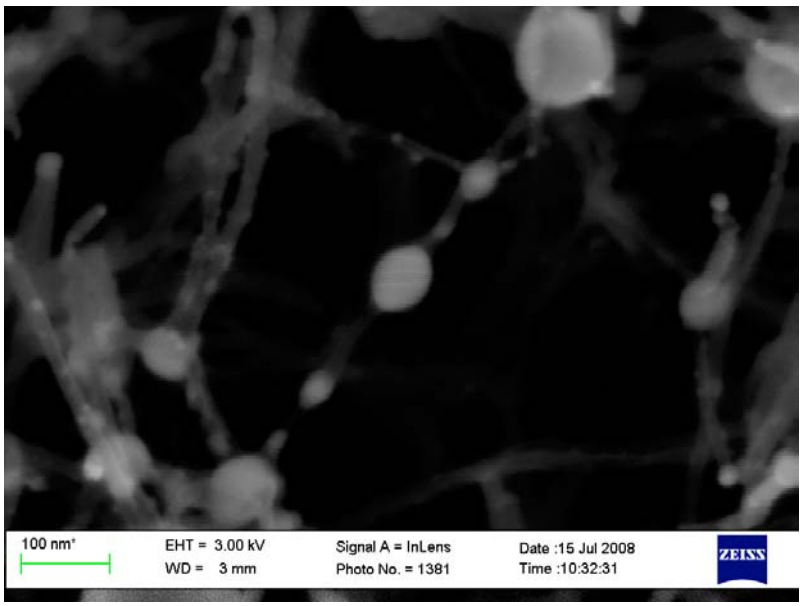



Fig. 5. Multiwall CNT covered by metal by means of laser ablation technology

After preliminary test the contact angle between multiwall carbon nanotubes and metals was measured by scanning electron microscopy unit SUPRA 55 (Carl Zeiss). Material properties of contact media for CNM were measured by microanalyse system INCA 350. It was shown that specific surface energy parameters for carbon nanomaterials can be measured correctly. Direct method (by electron microscopy) and indirect method (by measuring of contact angle of bidistilled water on CNM coating) were provided, comparison shows a good correspondence. Obtained results can be useful for study of chemical bonds of CNM with different materials under tests.

**References**

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