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SURFACE ENERGY HETEROGENEITY PROFILES OF CARBON NANOTUBES WITH A COPOLYMER-MODIFIED SURFACE USING SURFACE ENERGY MAPPING BY INVERSE GAS CHROMATOGRAPHY

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The effectiveness and quantitative control of the surface transition of multi-walled carbon nanotubes (MWCNTs) was characterized by inverse gas chromatography (iGC). The surface energy profile of carbon nanotubes compatibilized with an olefin-maleic-anhydride-ester-amide (OMAEA)-type coupling agent was determined by a surface energy analyzer (SEA). The surface energetic heterogeneity with energy distributions of dispersive and specific (acid-base) components of the surface energy of the MWCNTs were determined at various surface coverages. The results of the surface energy mapping showed that surface treatment significantly reduced the dispersive surface energy of MWCNTs and increased the specific surface energy. Furthermore, the surface modification enhanced its Lewis basic character and simultaneously decreased the acidic character of MWCNTs. It has been demonstrated that the surface treatment modified the heterogeneity profiles of the energetic surface of the carbonaceous nanomaterials.

Keywords: carbon nanotubes, surface treatment, inverse gas chromatography, surface energy analysis

1. Introduction

Carbon nanotubes (CNTs) can serve as excellent candidate materials for uses in numerous industrial applications because of their considerable advantages. CNTs are one of the best reinforcing constituents for nanocomposites [1] and hopefully catalytic metal–support in heterogeneous catalysis [2]. CNTs could replace the common catalyst supports of Ni/Mo-catalysts used in the production of fuel components of engine fuels with high hydrogen contents in their molecular structures [3]. Carbon nanotube-supported Co/Mo-catalysts with different Co/Mo atomic ratios were successfully used in the hydrocracking reaction of the vacuum residue of crude oil from Gudao oil field [4]. In the Fischer–Tropsch process (FTP), CNTs that supported transition metal catalysts are used to increase catalytic activities. An excellent study of FTP on Co catalysts supported by CNTs was reported by Tavasoli et al. [5]. Chen et al. [6] demonstrated that Fe nanoparticles encapsulated in CNTs are promising catalyst in FTP to synthesize light olefins. The catalytic consequence of hydrothermal liquefaction of microalgae to produce bio-oil over CNT-supported transition metal (Co, Ni, Pt) catalysts was reported by Chen et al. [7].

To change the wettability and chemical character of the CNTs or to avoid agglomeration in nanocomposites, the CNT surfaces are often exposed to surface functionalization [2] and modification processes using polyfunctional anchoring, capping, and coupling agents [8]. Research has shown that metal–support bindings can be strengthened by functional groups that are covalently bonded (grafted) to the support. Functionalized carbon nanotube-supported Pt nanoparticles were applied with favourable results in terms of selective olefin hydrogenation [9]. Because CNTs adsorb molecules well, functionalized CNTs are attractive chromatographic stationary phases for separation of normal and isoalkanes and aromatic compounds in the development of alternative fuels with high hydrogen/carbon ratios [10].

However, non-covalent functionalization using coupling agents or compatibilizers does not perturb the structure of the carbon nanotubes, establishes proper interactions between carbon nanotubes and the polymer matrix, and prevents the formation of nanotube agglomerates [11]. In terms of the properties of the reinforced composites of CNTs, the couplings between the nanotubes and the matrix are important beside the mechanical properties of the building parts [12]. These interactions depend on the surface properties and energies of the two materials. The surfaces of chemically derivatizated CNTs were investigated by means of various ana-

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lytical methods, e.g. thermal analysis [9-10,13-14], infrared spectroscopy (IR) [10,13], transmission electron microscopy (TEM) [13,16], Raman [16] and atomic force microscopy [10], and inverse gas chromatography (iGC).

iGC is a precise analytical method which is suitable for determining the surface energetic characteristics of the CNTs [13,15-17]. iGC was used for the characterization of the chemical character of the surface and was utilized to measure dispersive and specific surface energies, of numerous CNT substances [18]. The quantitative characterization of surface functionalization by surface energy mapping is of great importance. However, previous papers have presented surface energy values for functionalized CNTs over unclear surface coverages without energetic profiles and surface energy distribution functions, which, therefore, could not give correct information on the surface of the CNTs.

In this study, the dispersive, specific (acid-base) components of the surface energy with their heterogeneity charts and energy probability density functions of untreated and compatibilized MWCNTs are presented. A comparative quantitative characterization of the effectiveness and quantitative control of surface treatment is given. The exclusive energy scaling of the surfaces of the MWCNTs by energy heterogeneity charts with surface energy probability density functions over wide surface coverages is the new approach and main novelty of this paper.

2. Experimental and Methods

2.1. Samples and Measurements

Multi-walled carbon nanotubes (MWCNTs) were manufactured at 973 K by the chemical vapour deposition (CVD) process over a Fe/Co bimetallic catalyst at the Department of Chemical Engineering Science (University of Pannonia, Veszprém, Hungary) [19]. Their diameter was between 10 and 20 nm and their average length was above 30 µm.

An olefin-maleic-anhydride-ester-amide (*Fig.1*) copolymer (OMAEA) was used as a compatibilizer. The coupling agent was synthesized at the Department of MOL Hydrocarbon and Coal Processing (University of Pannonia, Veszprém, Hungary). The surface of MWCNTs was covered by the compatibilizer from a hydrocarbon solution of the coupling agent while the mixture was stirred for 1 hour at 333 K. The solvent was subsequently evaporated and the treated MWCNTs were dried at 383 K for 2 hours in air [11].

The surface energies of as-received and compatibilized samples of MWCNTs were measured by a Surface Energy Analyzer (iGC-SEA, Surface Measurement Systems Ltd., Alperton, UK) over a series of surface coverages from $(n/n_m) = 0.005$ to $(n/n_m) = 0.030$. iGC samples were produced by filling 20-25 mg of CNTs into silanized Pyrex glass tubes of I.D. = 3 mm under a vacuum and moderate vibration. The samples of MWCNTs were stabilized in the column with plugs of silanized glass wool. The samples were preconditioned in the column at the actually measured temperature for 60 minutes before each measurement. The iGC experiments were carried out at a column temperature of 353 K, with a Helium carrier gas flow of 10 cm^3/min. Methane gas was used as a dead-time marker using a flame ionization detector; and n-hexane, n-heptane, n-octane, n-nonane, chloroform and toluene as test compounds. The surface energy values were estimated using the specific retention volumes of the test compounds [20].

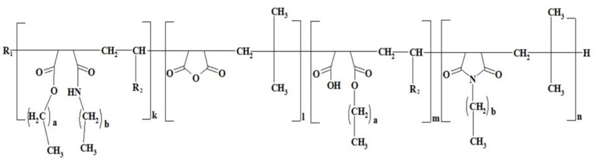

Figure 1. Structure of the olefin-maleic-anhydride-ester-amide copolymer (OMAEA) coupling agent, where R1: alkyl chain with length of the olefinic monomer; R2: alkyl chain with R1–2 carbon number; a, b: 2–21; k: 0.2–2; l: 1–7; m: 1–7 and n: 0.3–2 [11]

The specific retention volumes were obtained from the adjusted retention times:

$$V_w = t'_{\mathrm{R}} \dot{V}_{\mathrm{c}} / m_{sp} \tag{1}$$

The mean flow rate of the carrier gas in the column, $\dot{V}_{\mathrm{c}}$, was evaluated as given in Ref. [20].

2.2. Theoretical Methodologies

The dispersive component of the surface energy ($\gamma_{\mathrm{s}}^{\mathrm{d}}$) and its heterogeneity profile of samples of MWCNTs were calculated using the Dorris-Gray method [21] over different surface coverages:

$$\gamma_{\mathrm{s}}^{\mathrm{d}} = \frac{1}{4\gamma_{\mathrm{CH_2}}} \left(\frac{RT \cdot \ln\left(V_{w,n\mathrm{C}+1} / V_{w,n\mathrm{C}}\right)}{N \cdot a_{\mathrm{CH_2}}} \right)^2 \tag{2}$$

When plotting $RT\cdot\ln(V_{w,n\mathrm{C}})$ against carbon number, nC, for the n-alkane probes, a straight line is generated from the gradient from which the dispersive free energy of the sample surfaces of the MWCNTs, $\gamma_{\mathrm{s}}^{\mathrm{d}}$, can be calculated.

The specific (Lewis acid-base) surface energy $\gamma_{\mathrm{s}}^{\mathrm{ab}}$ of samples of MWCNTs was calculated from the basic component (γ_{s}^{-}) and the acidic component (γ_{s}^{+}) of the surface energy:

$$\gamma_{\mathrm{s}}^{\mathrm{ab}} = 2 \cdot \sqrt{\gamma_{\mathrm{s}}^{+} \gamma_{\mathrm{s}}^{-}} \tag{3}$$

The basic and acidic components of the surface energy were obtained from the specific parts of free enthalpy changes of adsorption $\Delta G_{\mathrm{ads},i}^{\mathrm{ab}}$ of polar probes i:

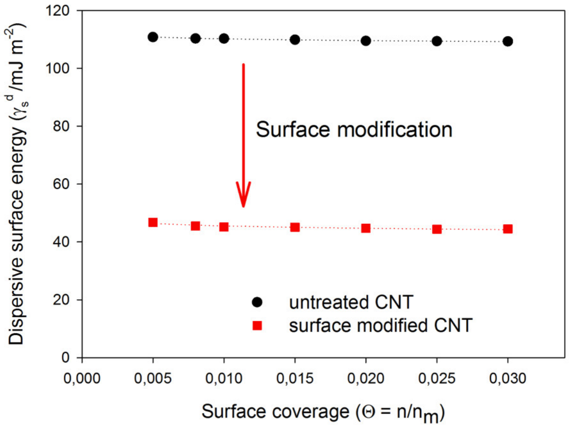

Figure 2. Dispersive surface energy profiles of untreated samples of MWCNTs and those treated with an olefin-maleic-anhydride-ester-amide copolymer (OMAEA) coupling agent compatibilized at 353 K and over various surface coverages (the dotted correlation lines are only to improve visualization).

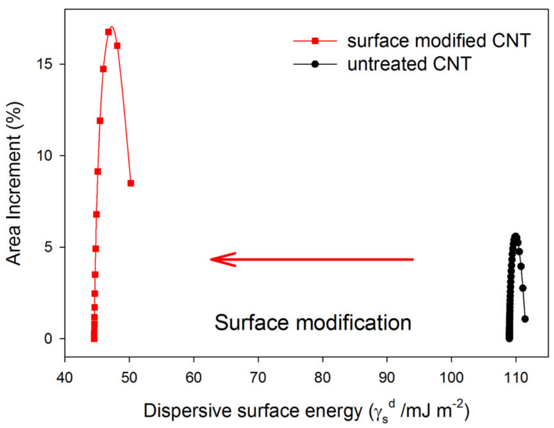

Figure 3. Dispersive surface energy probability functions of untreated samples of MWCNTs and those treated with an olefin-maleic-anhydride-ester-amide copolymer (OMAEA) coupling agent compatibilized at 353 K (the solid correlation lines are only to improve visualization).

$$\Delta G_{\mathrm{ads},i}^{\mathrm{ab}} = 2N \cdot a_i \cdot \left(\sqrt{\gamma_i^{+} \gamma_{\mathrm{s}}^{-}} + \sqrt{\gamma_i^{-} \gamma_{\mathrm{s}}^{+}} \right) \qquad (4)$$

applying the van Oss-Chaudhury-Good theory [22] with the Della Volpe scale [23]. The specific free energy changes of adsorption of the polar probes were obtained as suggested by Donnet et al. [24].

3. Results and Analysis

3.1. Experiments

The dispersive surface energy profiles of the untreated samples of MWCNTs and those treated with the olefin-maleic-anhydride-ester-amide copolymer (OMAEA) coupling agent compatibilized at 353 K and over low surface coverages (n/n_{m}) are presented in *Fig.2*. The energy profiles show reasonable devaluation of dispersive surface energy for MWCNTs after surface modification detected by *n*-alkane molecular probes: the dispersive surface energy ($\gamma_{\mathrm{s}}^{\mathrm{d}}$) of the MWCNTs decreased to half of its initial value.

The untreated samples of MWCNTs exhibited dispersive surface energies of ~110 mJ/m^2 at 353 K, which is comparable to the values reported by other researchers studying carbon nanotubes [13-15] and graphitic carbon materials [25]. The relatively high values of the dispersive surface energy of untreated MWCNTs can be attributed to a strong nonpolar interaction potential to build physical long-range Keesom, Debye, and London attractions, which explains their high tendency to agglomerate [14]. However, the anchoring of olefin-maleic-anhydride-ester-amide (OMAEA) up on the MWCNTs surface caused a marked decrement in dispersive part of surface energy from ~110 mJ/m^2 to ~48 mJ/m^2 at 353 K. The large drop in the value of $\gamma_{\mathrm{s}}^{\mathrm{d}}$ of surface-treated MWCNTs shows that the dispersive surface energy of MWCNTs has been obviously altered by the coupling agent.

The surface treatment also affected the dispersive surface energy heterogeneity profile of the MWCNTs. The surface energy mapping of the samples of MWCNTs indicated that the dispersive components of surface energies of untreated samples of MWCNTs are almost constant within the region of low surface coverage. Consequently, the surface of the untreated MWCNTs can be considered quasi-homogeneous. However, the dispersive surface energy heterogeneity profiles of the treated MWCNTs prove that the copolymer-modified MWCNT surface is energetically slightly heterogeneous, because the dependence of $\gamma_{\mathrm{s}}^{\mathrm{d}}$ on surface coverage is relatively strong within the region of low surface coverage.

In addition, the distributions of the dispersive surface energies (*Fig.3*) obtained by point-by-point integration of dispersive surface energy profiles over the investigated range of the surface coverage support in a more illustrative manner also results in an increase in the dispersive surface energy heterogeneity. The dispersive surface energy probability function of the MWCNTs became more spread out after modification of the surface indicated a greater degree of energetic surface inhomogeneity.

The specific surface energy ($\gamma_{\mathrm{s}}^{\mathrm{ab}}$) profiles of the untreated samples of MWCNTs and those treated with OMAEA compatibilized at 353 K and over various surface coverages (n/n_{m}) are presented in Fig. 4. The untreated samples of MWCNTs possess specific surface energy of ~10 mJ/m^2 at 353 K, which value is near to that given by Lou et al. (8.84 mJ/m^2) for pristine carbon nanotubes at 373 K and over undefined degrees of surface coverage [14]. The quantitative surface energy analysis obtained by iGC-SEA methodology demonstrated that surface treatment of MWCNTs resulted in

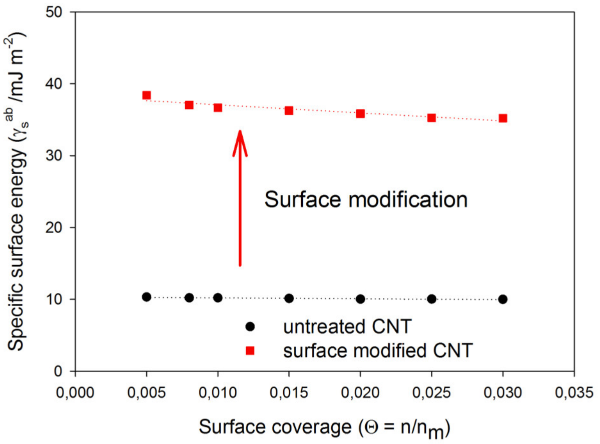

Figure 4. Specific surface energy profiles of untreated samples of MWCNTs and those treated with an olefin-maleic-anhydride-ester-amide copolymer (OMAEA) coupling agent compatibilized at 353 K and over various surface coverages (the dotted correlation lines only improve visualization).

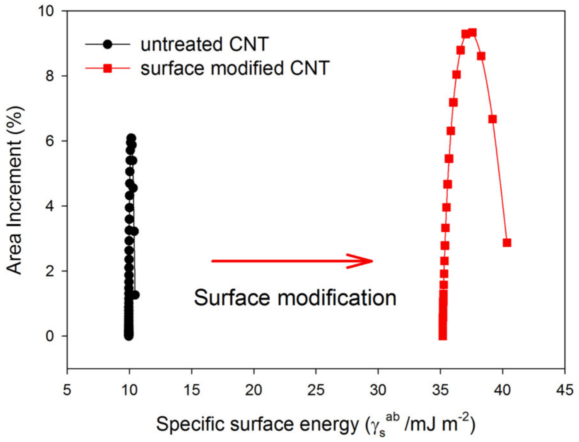

Figure 5. Specific surface energy probability functions of untreated samples of MWCNTs and those treated with an olefin-maleic-anhydride-ester-amide copolymer (OMAEA) coupling agent compatibilized at 353 K (the solid correlation lines only improve visualization).

significant changes in surface energies: the specific surface energy of CNT surfaces increased more than fourfold, from ~10 mJ/m^2 to ~41 mJ/m^2.

Furthermore, the dependence of γ_s^{ab} on surface coverage is pronounced for the compatibilized samples of MWCNTs which indicates that energetic heterogeneity attributed to chemical heterogeneity and the existence of electron donor-acceptor atomic groups on the surface. However, the quasi-constant specific component of surface energy for untreated MWCNTs suggests an energetically homogeneous surface and the absence of high specific energy surface sites.

The specific surface energy values of compatibilized MWCNTs are much higher than those of the untreated surfaces, declared the enhanced connection between compatibilized MWCNTs and polar analytes. The observed diversity in specific surface energies is accomplished from the adsorbed polar atomic clusters: namely the moderately electron-withdrawing maleic anhydride groups; and the electron-donating ester and amide groups with different nucleophilic or electrophilic characteristics.

The specific surface energy distributions in Fig. 5 represent the heterogeneity of the samples of MWCNTs and reveal that the untreated MWCNTs exhibited γ_s^{ab} values which varied from 9.9 to 10.3 mJ/m^2. This small variation in the specific surface energy demonstrated a fairly energetically homogeneous surface for untreated MWCNTs. However, as surface treatment increased the concentrations of polar clusters on the surface of MWCNTs, the modified surface exhibited great variations in γ_s^{ab} (from 37.3 to 42.9 mJ/m^2), implying that the compatibilized MWCNTs are surface energetic heterogeneous.

The surface treatment also modified the chemical characteristics of the MWCNTs. The acid-base surface energy mapping of the samples of MWCNTs (*Figs.6* and *7*) indicate that both the electron-accepting and donating abilities of the MWCNTs were raised appreciably after compatibilization of untreated MWCNTs consistent with the adsorption of electron-withdrawing and electron-donating atomic groups on the surface. The untreated samples of MWCNTs possess base surface energy of ~16 mJ/m^2 at 353 K, which value is near to that given by Lou et al. (12.97 mJ/m^2) for pristine carbon nanotubes at 373 K and over undefined surface coverage [14].

The surface energy mapping using the iGC-SEA methodology confirms that the surface treatment of MWCNTs raised the basic component (γ_s^-) of surface energy of MWCNTs: it resulted in a sevenfold increase from ~16 mJ/m^2 to ~112 mJ/m^2. The acidic component of surface energy γ_s^+ of untreated samples of MWCNTs was measured as ~1.7 mJ/m^2 at 353 K, which is in good agreement with that reported by Lou et al. (1.51 mJ/m^2) for pristine carbon nanotubes at 373 K and over undefined surface coverages [14]. The surface modification of MWCNTs resulted in a more than twofold increase in the value of the acidic component (γ_s^+) of the surface energy of MWCNTs from ~1.7 mJ/m^2 to ~3.7 mJ/m^2.

However, the profiles of acid-base surface energy heterogeneity of the treated MWCNTs also prove that the copolymer-modified MWCNT surface became energetically more heterogeneous, because the dependencies of γ_s^- and γ_s^+ on surface coverage are relatively stronger than those of the untreated MWCNTs. The presence of non equi-energetic active surface centers exposes that the surfaces of the compatibilized MWCNTs are not energetically uniform for specific acid-base interactions and the surface treatment considerably altered the ability of MWCNTs to connect with molecular species by specific interactions.

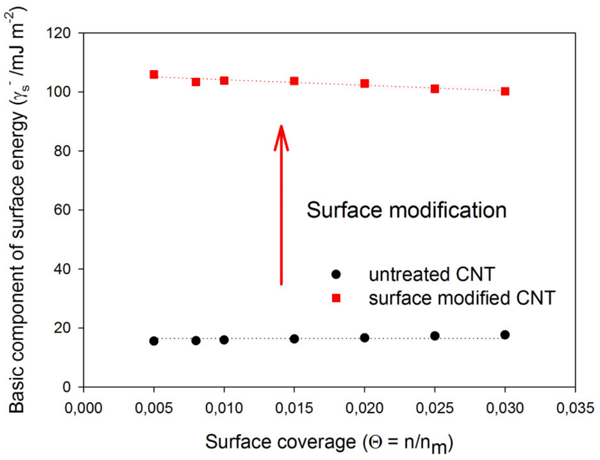

Figure 6. Basic component profiles of surface energy of untreated samples of MWCNTs and those treated with an olefin-maleic-anhydride-ester-amide copolymer (OMAEA) coupling agent compatibilized at 353 K and over various surface coverages (the dotted correlation lines only improve visualization).

The larger change in the base component of the surface energy (γ_s^-) after compatibilization with a polyalkenyl-poly-maleic-anhydride-ester-amide additive indicates a higher concentration of electron-donating ester and amide groups on the surface. The large value of γ_s^- (relative to γ_s^+) implies a more basic characteristic and donor properties of the surface of the treated MWCNTs.

4. Conclusion

The experimental data demonstrated that iGC is a useful methodology of characterizing the variation in the surface characteristics of MWCNTs after non-covalent functionalization. The exclusive energy scaling of the SEA methodology using energy heterogeneity charts with surface energy probability density functions over wide surface coverages presents profitable additional information on the differences in terms of the nature, homogeneity and heterogeneity of surface energies resulting from surface transformations. The multilateral surface energy analysis of SEA presents a quantitative control of the effectiveness of surface treatment and demonstrates the importance of the dependence of surface energy analysis on coverage.

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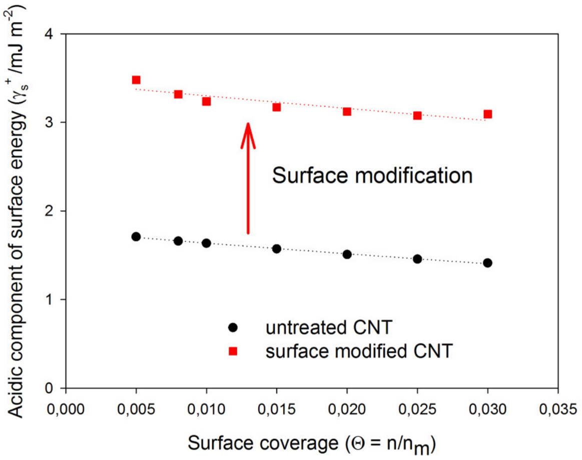

Figure 7. Acidic component profiles of surface energy of untreated samples of MWCNTs and those treated with an olefin-maleic-anhydride-ester-amide copolymer (OMAEA) coupling agent compatibilized at 353 K and over various surface coverages (the dotted correlation lines only improve visualization).

SYMBOLS

$a_{\mathrm{CH_2}}$, a_i	cross sectional area of an adsorbed methylene group and of probe *i*
$\Delta G^{\mathrm{ab}}_{\mathrm{ads},i}$	specific free enthalpy of adsorption
m_{sp}	mass of the adsorbent in the column
N	Avogadro's number
R	gas constant
T	temperature
t'_{R}	adjusted retention time
$\dot{V}_{\mathrm{c}}$	mean flow rate of the carrier gas
V_w	specific retention volume
$\gamma_{\mathrm{s}}^{\mathrm{ab}}$, $\gamma_{\mathrm{s}}^{\mathrm{d}}$	specific and dispersive parts of the surface energy of solid sample material
$\gamma_{\mathrm{CH_2}}$	surface energy of a methylene group
γ_{s}^{+}, γ_{s}^{-}	acid-base components of the surface energy of solid sample material
γ_i^{+}, γ_i^{-}	acid-base components of the surface tension of polar liquid probe *i*
$\Theta=n/n_{\mathrm{m}}$	surface coverage

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