iGC SEA Application Note 226

Surface Energetic Heterogeneity of Carbon-based Nanomaterials

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Surface energy is a useful parameter describing the energetic properties of the surface of a solid sample. Inverse gas chromatography (IGC) is an established and versatile tool in determining the surface free energy of solids by adsorption of vapours with known properties. Second generation IGC instrument: iGC SEA is proven to be an efficient and accurate energy mapping technique, generating highly reproducible surface energy data. Surface energetic heterogeneity of commercial multi-walled carbon nanotubes was measured by iGC SEA, relating to the effects of different modification treatments.

Introduction

Surface energy is an important property in numerous industrial application and processes. It shows a strong dependency on various macroscopic properties and relates to many crucial interfacial phenomena, i.e. adhesion and wetting behaviors.

The study and applications of nanomaterials such as carbon nanotubes (CNTs) have gained tremendous interest in recent years, due to their exceptional structural, electrical and mechanical properties [1-3]. Structurally, CNTs can be described as a sheet of graphene rolled into a tube, and vary by the number of carbon layers in their sidewalls; i.e. single-walled, double-walled and multi-walled [3]. CNTs however are often energetically inhomogeneous, exhibiting various surface sites, such as structural defects or specific functional groups. Therefore, a surface energetic heterogeneity profile can provide more comprehensive information on the nature and population of these surface sites [4]. Such a

heterogeneity profile allows the prediction of product properties, especially in the formulation of blends, composites or coatings.

Despite the potential importance of heterogeneity profiles, until now, there has been little emphasis on the characterization of the surface energy distribution of nanomaterials. Recent advances of IGC surface energy methodology allow for the determination of the aforementioned surface energy distribution [4,5], from the adsorption isotherms of a series of n-alkanes at finite concentrations.

iGC Surface Energy Analyzer (SMS, Alperton, UK) adopts this new approach and is equipped with the state-of-the-art injection technology which allows the precise control of the injection size. If a series of concentration (mole, n) of dispersive and polar probe vapors are injected at the same surface coverage (n/nm) , the dispersive surface energy and specific free energy at that particular surface coverage can be determined. Consequently, the injections of probe vapour at different surface coverages will result in a distribution of surface energy as a function of

surface coverage, which is referred as a surface energy profile. The determination of surface energy heterogeneity by iGC SEA can, therefore, be described as a mapping technique.

In this work, the surface energetic heterogeneity of commercial multi-walled CNTs was measured, relating to the effects of different modification treatments (i.e. annealing and oxidation).

Method

Material – Multi-walled Carbon Nanotubes

Commercial, multi-walled CNTs were used as received (Arkema SA, Lacq-Mourenx, France). These MWCNTs were synthesized by chemical vapour deposition, having outer diameters of ~10-20 nm and lengths of at least a few μm.

As-received MWCNTs were modified by:

i.   high temperature annealing (treatment at 2100 ºC for 2 hours under argon flow; CNTs were cooled to room temperature under argon and then exposed to air) and;

ii.   thermal oxidation (short treatments at 640 ºC under air flow).

Both as-received and surface modified CNTs were subjected to conventional characterisation techniques, e.g. electron microscopy, spectroscopy, thermal analysis etc. Sample preparation methods and details of each analytical method were reported elsewhere [6].

Surface Energy Heterogeneity

All analyses were carried out using iGC SEA (SMS, Alperton, UK) and the data were analysed using the standard SEA Analysis Software. 10 mg of MWCNTs samples were packed into individual iGC glass column (300 mm long by 3 mm inner diameter).

Samples were run at a series of surface coverages with alkanes and polar probe molecules to determine the dispersive surface energy distribution as well as the specific (acid-base) surface energy distribution. For the

analysis, the Dorris and Gray method was employed for dispersive surface energy component [7]. Specific contribution was determined by first measuring the free energy of desorption of a pair of mono-functional acidic and basic probe molecules, based on the polarisation approach [8] and Della Volpe scale [9].

Four n-alkanes: nonane, octane, heptane and hexane; and six polar probes: toluene, dichloromethane, ethyl acetate, chloroform, acetone and ethanol were used in this work. Each sample column was conditioned in-situ at 150 ºC and 0% RH with a Helium carrier gas flow of 10 sccm prior to every injection. All solvent injections were conducted at 100 ºC and 0% RH, with the same carrier gas flow rate. Inert methane gas was used for dead volume corrections.

Results

Effect of Different Modifications on MWCNTs

Figure 1 shows the TEM and SEM images of as-received, annealed and oxidised MWCNTs. It can be observed that all three samples exhibit similar diameters (10-20 nm) and texture (unaligned, wavy, morphology), typical for commercially produced MWCNTs [6, 10].
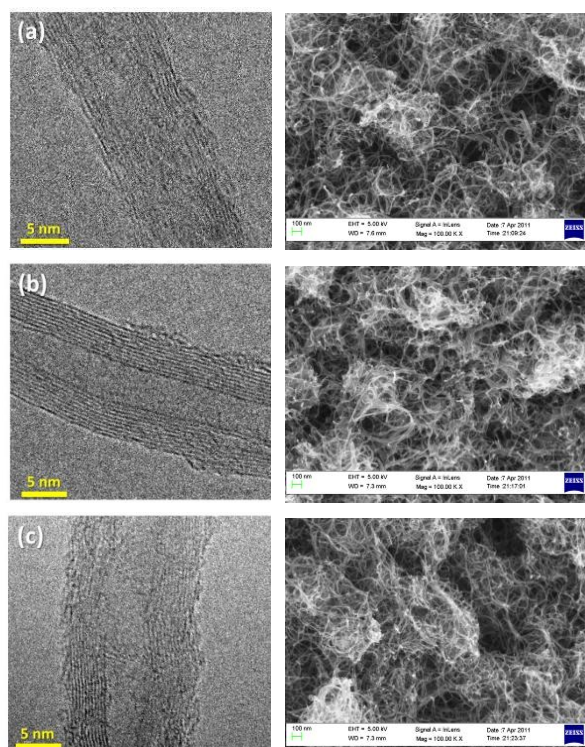
Figure 2. Dispersive surface energy profiles.

However, as-received and modified MWCNTs differ in their chemical and local structural surface properties, as determined by conventional analytical methods (Table 1). Annealed MWCNTs exhibited higher graphitic crystallinity, meanwhile, thermal oxidation increased the surface oxygen content, confirming the introduction of additional surface groups.

Table 1: *General characterisation data for as-received and modified MWCNTs**

MWCNTs	BET specific surface area [m²/g]	Raman spectra – Crystallinity I_G/I_D ratio	XPS – Surface oxygen content [atom %]
As-received	237	0.94 ±0.02	0.5
Annealed	215	1.33 ±0.03	0.6
Oxidised	256	0.89 ±0.03	1.4

*Published in [6].

Dispersive Surface Energy Heterogeneity

Dispersive surface energy (γ_S^D) profiles in Figure 2 show that all MWCNT samples were energetically heterogeneous (meaning that γ_S^D value changes with surface coverage). However the degree of energetic heterogeneity was found to depend on the modification treatment, with oxidised MWCNTs found to be energetically most active and most heterogeneous.

All MWCNT samples exhibited considerably high dispersive surface energies (~90 mJ/m² and above) concurring to a typical value for graphitic carbon materials [11]. γ_S^D results here demonstrate that IGC technique can be useful in determining subtle differences between the MWCNTs. It is also well recognised that energetic surface heterogeneity can have a significant impact on the thermodynamic characterisation of carbon surfaces [12] and often this is discussed in the context of wetting hysteresis [13].
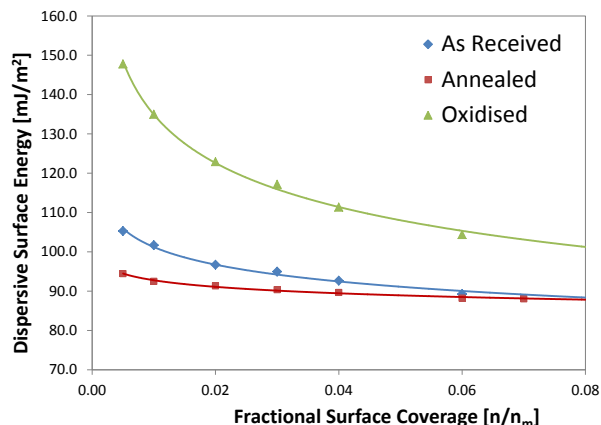
In order to represent the heterogeneity of the samples in more illustrative manner, the surface energy distributions are obtained by a point-by-point integration of the surface energy profiles, resulting in plot of γ_S^D versus *percentage of surface (area increment),* as shown in Figure 3.
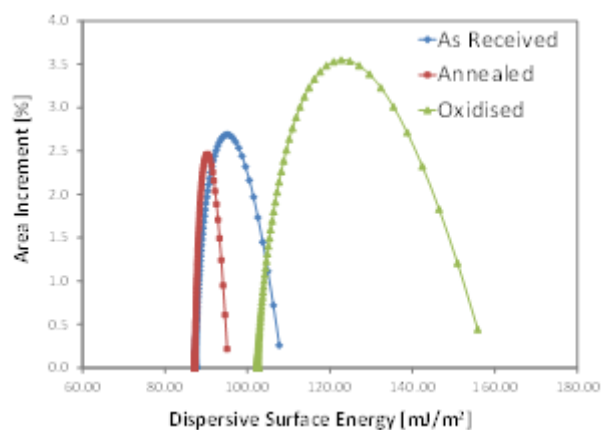

Figure 3. Dispersive surface energy distributions

Energy distributions in Figure 3 reveal that as-received MWCNTs had γ_S^D values which varied from ~ 87 to ~107 mJ/m². As thermal annealing increased the crystallinity of MWCNTs, the annealed surface only possessed small variations in γ_S^D (~87 to ~95 mJ/m²), implying a fairly homogeneous surface property. Though γ_S^D values of as-received and annealed samples differ at lower surface coverages (less than 6%), their γ_S^D converge at higher surface coverages. This highlights the importance of measuring surface energetic heterogeneity profile for real solids.

Contrasting to the other two samples, oxidised MWCNTs had a much wider range of γ_S^D values, varying from ~102 to ~155 mJ/m^2. This may be due to the introduction of additional surface functional groups with high γ_S^D, the creation of structural defects (such as micropores and graphene edges), and the opening of initially closed MWCNTs during the thermal oxidation process.

Surface Polarity and Acid-Base Surface Chemistry of MNCNTs

Figure 4 shows the acid-base (specific) surface energy (γ_S^{AB}) profiles of all three MWCNT samples, determined from chloroform (monopolar acid) and toluene (monopolar basic). Although γ_S^{AB} values were determined using only two monopolar probes (making the values more probe molecule dependent), they provide a relative assessment of the MWCNTs' potential to undergo specific interactions.
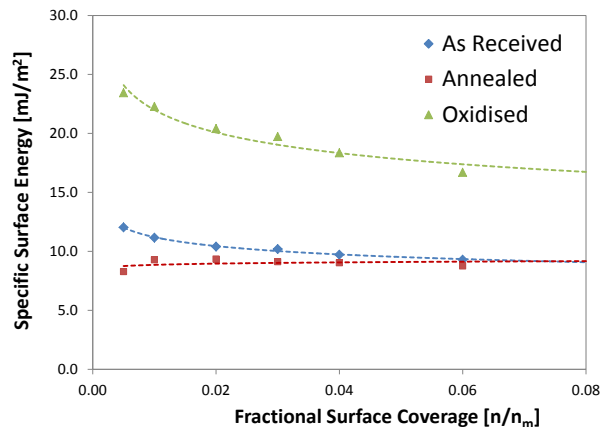

Figure 4. Specific (acid-base) surface energy profiles.

Evidently shown here, oxidised MWCNTs had relatively higher concentration of Lewis acid-base functional groups on the surfaces, with almost 80% increment in γ_S^{AB} values comparing to the as-received MWCNTs. γ_S^{AB} of as-received MWCNTs was marginally higher than that of annealed MWCNTs. Similarly, if the surface polarity of these MWCNTs were presented in term of percentage of $\gamma_S^{AB}/\gamma_S^{Total}$ (Figure 5), oxidised MWCNTs clearly have the highest surface polarity, followed by the as-received and annealed samples.
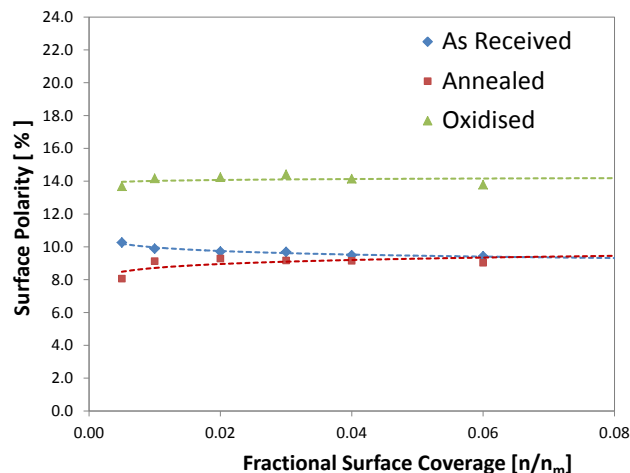

Figure 5. Surface polarity (%) profiles.

Specific Gibbs free energy of desorption ΔG_{SP} also changes with surface coverages, indicating the heterogeneous nature of these samples. Oxidised MWCNTs in particular exhibit stronger interactions with the polar probes, as depicted in Figure 6, in agreement with their higher surface polarity, discussed above.

Higher ΔG_{SP} values can be attributed to a higher concentration of polar surface groups or different surface groups with higher specific surface energy. All samples show some degree of interactions with all polar probes, but predominantly interact with ethanol and acetonitrile probes. Both ethanol and acetonitrile are bi-functional probes, with the former being slightly acidic and the latter being slightly basic. Stronger interactions with these bi-functional polar probes imply that MWCNTs are amphoteric in nature.
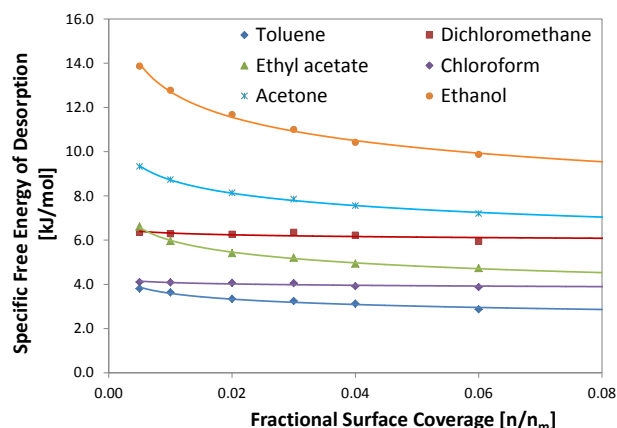
Figure 6. Specific free energy of desorption of six different polar probes with Oxidised MWCNT samples.

Surface chemistry of all MWCNTs was assessed using the Gutmann acid (K_a) and base (K_b) numbers, determined based on the Gutmann concept. Values for each sample were calculated using the ΔG_{SP} values of polar probes at that particular surface coverage.

Figure 7 presents the K_b (Lewis basicity) and K_a (Lewis acidity) profiles for all samples. Results clearly show that the K_b for all samples is consistently higher than K_a, indicating that the surfaces of these MWCNT samples are more basic in nature. This means that surfaces of sample possess higher concentrations of electron-donating surface functional groups.
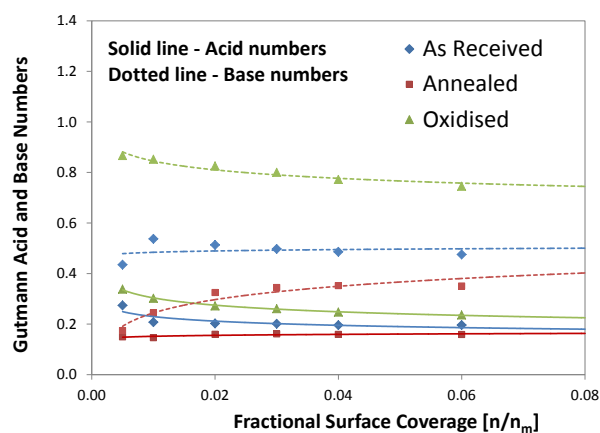

Figure 7. Gutmann acid and base numbers profiles.

Results presented here clearly indicate that energetic heterogeneity and homogeneity of the as-received and surface modified MWCNT samples can be easily distinguished by IGC

technique. This is very important to differentiate any subtle differences in surface physical and/or chemical conditions of a wide range of solid materials.

In summary, IGC was proven as a powerful and sensitive technique for assessing the surface energy and surface chemistry of carbon-based nanomaterials. This work demonstrates the importance of determining surface energies in dependence of coverage, e.g. through the measurement of surface energy profiles, in order to fully characterise the often pronounced difference in energetic heterogeneity of real solid surfaces.

Using such energy mapping techniques, IGC can reveal specific changes in surface character, e.g. surface polarity or acid-base surface chemistry, that are not readily accessed by other conventional techniques, but which are highly relevant to both processing and application of CNTs. This work also highlights applicability of IGC technique to characterise a wide range of CNTs, and nanomaterials with large accessible surface areas, in general.

Conclusion

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