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]. These nanomaterials however are often energetically inhomogeneous, exhibiting a wide range of lower and higher energy sites. Therefore, a surface energetic heterogeneity profile can provide more comprehensive information on the nature and population of these surface sites [4]. Finite concentration Inverse Gas Chromatography (IGC) experiments allow for the determination of the aforementioned surface energy distributions which more accurately describe the anisotropic surface energy for real materials [4]. In this work, the surface energy heterogeneity of commercial multi-wall CNTs was measured, relating to the effects of different modifications (i.e. annealing and oxidation).

### Materials & Methods

#### Preparative Techniques
- Commercial multi-walled carbon nanotubes (MWCNTs) were used as received (Arkema SA, Serquigny, France).
- Modifications on MWCNTs [5]:
  1. by high temperature annealing (2100 °C under argon flow);
  2. by thermal oxidation (640 °C under air flow).
- All samples were characterized using transmission electron microscopy (TEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS).

#### Inverse Gas Chromatography for Surface Energy Mapping
- Surface free energy heterogeneity analyses were determined using IGC-SEA (Surface Measurement Systems Ltd., UK).
- Heterogeneity mapping was conducted at 100 °C with a Helium carrier gas flow rate of 10 sccm. All samples were conditioned in-situ at 150 °C prior to every solvent injections.

### Results & Discussion

#### 1. Effect of Different Modifications on MWCNTs
- Morphology of as received MWCNT (Figure 2) is relatively wavy and disorganised.
- Various characterization results (Table 1) confirmed significant differences in the modified MWCNTs’ surface properties compared to the as received sample.
- Annealing has increased crystallinity of MWCNT considerably, but decreased specific surface area.
- Oxidation increased surface oxygen content (by factor of 3), hence the surface polarity. However there was a slight decrease in crystallinity, with presence of additional defects.

![Fig. 2 HRTEM images of (a) As received, (b) Annealed, and (c) Oxidized MWCNTs](image)

**Table 1. General characterization data for as-received and modified MWCNTs [5]**

<table>
<thead>
<tr>
<th>MWCNT</th>
<th>BET specific surface area [m²/g]</th>
<th>Raman spectra - Crystallinity (I/D) ratio</th>
<th>XPS - surface oxygen content [atom %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>237</td>
<td>0.94 ±0.02</td>
<td>0.5</td>
</tr>
<tr>
<td>Annealed</td>
<td>215</td>
<td>1.33 ±0.03</td>
<td>0.6</td>
</tr>
<tr>
<td>Oxidized</td>
<td>256</td>
<td>0.89 ±0.03</td>
<td>1.4</td>
</tr>
</tbody>
</table>

#### 2. Dispersive Surface Energy Heterogeneity
- IGC dispersive surface energy (\(\gamma^D\)) mapping – ability to distinguish homogeneity and heterogeneity in surface energy.
- \(\gamma^D\) profiles in Figure 3 show that all MWCNT samples were heterogeneous in surface property (meaning that \(\gamma^D\) changes with surface coverage); however the degree of energetic heterogeneity was found to depend on the modification treatment.
- Figure 4 reveal that high crystallinity (annealed) sample only possessed small variations of \(\gamma^D\), implying a fairly homogeneous surface property.
- Oxidized sample was energetically most active and heterogeneous (\(\gamma^D\) between 102 to 155 mJ/m²). This may be due to the creation of structural defects (such as micropores and graphene edges), and the opening of initially closed MWCNTs during the thermal oxidation process.

**Figure 3** Dispersive surface energy profiles

**Figure 4** Dispersive surface energy distributions

### Conclusions

Dispersive surface energy heterogeneity profiles were measured on as received, annealed and oxidized CNT samples. Thermal oxidation showed a dramatic effect on the surface property of CNTs, possibly due to the introduction of additional surface functional groups and/or structural defects. IGC has been demonstrated as a powerful technique for the study of CNT surface property and the effect of modification treatment. IGC can reveal specific changes in surface character that are not readily accessed by other techniques, but which are highly relevant to both processing and application of CNTs. This work also highlights the applicability of IGC technique to characterize other nanomaterials with large accessible surface areas.

### Bibliography