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Raman study of inhomogeneities in carbon nanotube distribution in CNT–PMMA composites

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This work is aimed at characterization of the carbon nanotube (CNT) distribution in polymethyl methacrylate (PMMA)–CNT composites by high-resolution Raman spectroscopy. In particular, we focus on study of the boundary regions between the CNT aggregates and the surrounding areas where the CNTs are well dispersed in the PMMA matrix. Different laser excitation energies (1.96 and 2.33 eV) were used to preferentially probe metallic and semiconducting SWCNTs, respectively. At both

photon energies, spectral line scans across the boundary regions were performed revealing a substantial drop in intensity of G^+ CNT Raman mode and an increase of the D/G^+ -intensity ratio. The latter testifies to a preferential dispersion of functionalized CNTs in the PMMA matrix. Certain inhomogeneities were observed by Raman spectral imaging even in the areas with well-dispersed CNTs.

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1 Introduction Since the identification of carbon nanotubes (CNTs) by Ijima in 1991 [1], this material has become a subject of great interest and effort in science because of the outstanding physical properties it exhibits. CNTs can be thought of as graphene sheets rolled into seamless cylinders of various diameters and in principle infinite length. Depending on the number of concentrically arranged tubes, CNTs are termed single-walled (SWCNT), double-walled (DWCNT), and multi-walled (MWCNT) CNTs. Moreover SWCNTs exist as semiconducting or metallic types, depending on the orientation of the hexagonal lattice relative to the tube axis, as classified by the chiral indices (n,m). Their extraordinary mechanical, electrical, thermal, and optical properties render them very attractive for a wide range of applications [2, 3] including advanced composite materials.

However synthesis of CNT-based composite materials still remains a big challenge. In particular it remains to overcome the difficulties in achieving good nanotube dispersion within the matrix material. The fact that present synthesis routes produce SWCNTs in a bundled state due to van der Waals intertube interaction is another serious hurdle,

as SWCNT bundles do not exhibit the excellent properties of their individual components. Thus special treatment has to be applied in order to break these bundles. In an ideal composite material, the individual SWCNTs would be homogeneously dispersed in the matrix. A second issue is the interaction between the CNTs and the host: to improve the load transfer between host and filler covalent linking between the two components is desirable.

One approach to solve these problems is functionalization of the CNT source material prior to its incorporation into the polymer matrix. Optimization is required to maximize the transfer from the polymer to the CNTs but minimize the number of wall defects created by the covalent grafting of the functional groups on the CNT sidewalls. Moreover appropriate functional groups have to be chosen to assure compatibility with the polymer being used.

In order to understand and improve the microstructure of CNT composites and relate it to mechanical, electrical, or thermal properties, advanced characterization methods have to be applied. Raman spectroscopy has proven to be a powerful tool for studying both pure CNT materials [2, 4–11] and CNT-based composites [12–16]. Synthesis of the

polymethyl methacrylate (PMMA) composite material used here, based on functionalized SWCNTs, was reported recently and its study revealed inhomogeneities in the CNT distribution within the polymer and associated degradation in the mechanical properties suggested as being attributed to the presence of CNT agglomerates [17, 18]. The CNT distribution in the samples was illustrated by Raman spectral mapping of the G^+ -peak intensity as a function of position.

The present work is aimed at investigation of the interface region between the SWCNT agglomerates and the areas with well-dispersed nanotubes in CNT-PMMA composites by Raman imaging and spectral line scanning across these areas. In addition, we examined inhomogeneities in the CNT distribution in the “dispersed” regions by following the G band/ PMMA Raman intensity ratio and downshift of the G band due to laser heating.

2 Experimental procedures After functionalization with phenyl-ester groups, SWCNTs were incorporated into a PMMA matrix by *in situ* polymerization [17]. A sample containing 0.097 wt.% functionalized SWCNT loading was used for this study.

Raman measurements were conducted with a WiTEC CRM 200 confocal Raman imaging system in a back-scattering geometry. In order to preferentially probe semiconducting or metallic SWCNTs and thus be able to distinguish any different behavior due to electronic structure, two different laser excitation wavelengths were used, namely 532 and 633 nm (corresponding to 2.33 and 1.96 eV, respectively). Raman spectra were collected using a 600 g/mm diffraction grating. The laser beam was focused on the sample surface onto a spot of 1 or 3.45 μm in diameter using a 100 $\times$ or 20 $\times$ objective, respectively. Laser powers were measured directly on the sample stage and were typically between 0.5 and 1.5 mW.

As illustrated in Fig. 1a, 2D spectral imaging allowed selecting large CNT agglomerates for further detailed examination. Raman line scans were performed starting within an agglomerate and ending in the dispersed area in order to study the boundary region. An example of such a scan – a resulting set of consecutive equally spatially separated Raman spectra – is presented in Fig. 1b. A piezo scanner permitted 1 μm scan steps.

3 Results and discussion Raman spectra from different CNT aggregates in the composite were acquired. All line scans showed the general features illustrated in Fig. 1b. Inside the agglomerated area no peaks related to the PMMA matrix are seen – only the CNTs contribute to the high intensity of the Raman spectrum. At some point a big drop in Raman intensity of the signal from CNTs occurs along with the appearance of peaks related to PMMA.

After acquisition, the Raman spectra were fitted by Lorentzian peak shapes. Typical peak fitting results of the Raman data from line scans in the aggregates of different sizes are presented in Fig. 2 for both the 1.96 and 2.33 eV excitation energies. It merits noting that the peak at 1330 cm^{-1} corresponds to a combination of the SWCNTs D-band and a small peak due to PMMA. From this point on, this combined peak will be denoted as D^* to discern it from the pure D-band peak of CNTs. The G^+ -peak intensity, the D^*/G^+ -intensity ratio and the intensity ratio of the D^* to the PMMA peak at 1450 cm^{-1} ($D^*/1450$ -intensity ratio) are plotted against the spatial position in Fig. 2. The $D^*/1450$ -intensity ratio was chosen because it reflects the contribution of the PMMA spectrum to the overall observed Raman spectrum of the composite. G^+ intensity and $D^*/1450$ ratio were normalized to their maximum values.

The Raman signal of CNTs (evidenced by the G^+ intensity in Fig. 2) is not only very inhomogeneous regarding different areas in the composite (agglomerated areas and dispersed areas) but also shows inhomogeneities in an agglomerated region itself in some cases (Fig. 2a). However at some given scan step a large drop in G^+ intensity occurs accompanied by the appearance and decrease of the $D^*/1450$ -intensity ratio. At the same time the D^*/G^+ -intensity ratio increases. After a certain transition region all three ratios stabilize at new levels. We attribute this transition region (indicated by broken lines in Fig. 2) to the boundary interface area between the agglomerates and dispersed areas.

The boundary interface width is found to be about 4 μm for an agglomerate of $\sim 30\text{ }\mu\text{m}$ big while it is about 20 μm wide for an agglomerate of $\sim 66\text{ }\mu\text{m}$ (Fig. 2a and b, respectively), which is indicative of its dependence on the agglomerate size. With 1.96 eV photon energy we probe predominantly the metallic nanotubes in our sample while the semiconducting ones are in resonance with 2.33 eV

Figure 1 (online color at: www.pss-b.com) Raman spectral map of maximum G^+ intensity in CNT-PMMA composite (a) indicating CNT aggregates (bright spots). The blue arrow denotes direction of the spectral line scan (b) starting in the aggregate and ending in the dispersed area. Each spectrum in (b) corresponds to one step scan of 1 μm . Spectra were collected at 1.96 eV photon excitation energy.

Figure 2 Raman data obtained from line scans through the aggregated/dispersed area boundary in different aggregates for (a) 1.96 eV and (b) 2.33 eV photon excitation energy. Symbol assignment: $I_{G^+}/I_{1450PMMA}$ (normalized to their maximum values) – empty squares and half filled triangles, respectively; I_{D^-}/I_{G^+} – filled circles; I_{D^-}/I_{G^+} (after subtraction of PMMA contribution) – empty circles. The interface regions between agglomerate (left side) and dispersed areas (right side) are indicated by vertical lines. Note different horizontal axis scale in (a) and (b).

photons. Analysis of the line scans across the boundary interface area does not reveal any significant difference in behavior of metallic versus semiconducting CNTs – both exhibit the same overall trends, i.e., drop of I_{G^+} while increase of I_{D^-}/I_{G^+} . However, the metallic nanotubes show a higher level of I_{D^-}/I_{G^+} both inside the agglomerates and in the dispersed area. This could indicate a higher degree of functionalization with phenyl-ester groups of metallic compared to the semiconducting CNTs as was shown earlier [4, 5].

As mentioned above both SWCNTs and PMMA show a peak at around 1330 cm^{-1} (Fig. 3), complicating the interpretation of the D^*/G^+ -intensity ratio. Since no PMMA peaks are observable in agglomerates, it can be assumed that this peak is only due to the CNT – signal, thus reflecting the real D band. However it is not trivial to separate the contribution of the CNT or PMMA signal to this peak in a boundary region or in the dispersed area of the composite as the PMMA contribution cannot be neglected in these cases.

Figure 3 Raman spectra of composite dispersed area before (1) and after (2) subtraction of pure PMMA spectrum (3). Spectra collected with 2.33 eV photon excitation energy.

This raises the question if the observed increase of the D^*/G^+ -intensity ratio could simply be due to an increase of the PMMA contribution to the spectrum. To address this issue, the PMMA contribution was removed from the composite spectrum by subtraction of a reference PMMA spectrum (Fig. 3) followed by new peak fitting. The resulting corrected D/G^+ values are shown together with the uncorrected ones in Fig. 2 for both excitation energies. The corrected D/G^+ values are indeed lower than the uncorrected values which demonstrates that the PMMA contribution cannot be neglected for dispersed regions. However the corrected values are still significantly higher than those observed in agglomerated areas. It can thus be concluded that the observed increase of the D/G^+ -intensity ratio going from agglomerated to dispersed regions is not due to only a higher PMMA contribution in the composite spectrum. With the corrected D/G^+ ratio the line scans can now be fully interpreted. Firstly the drop of G^+ intensity indicates a decrease of CNT concentration from agglomerate to dispersed region. Furthermore, the increase of the D/G^+ ratio indicates a higher defect level of the SWCNTs in the dispersed area. As functionalized CNTs are generally known to exhibit increased D-band intensities [4] this observation leads us to the conclusion that the fraction of functionalized CNTs is higher in the dispersed phase than in the agglomerates.

Further we observed inhomogeneities in the dispersed area itself as indicated by different G -band intensities relative to the PMMA peaks (Fig. 4).

Moreover these intensity variations are accompanied by a difference in the G^+ -peak position – a more intense G band exhibits a larger G^+ -peak downshift from its position in the source CNT material. Actually this observation holds not only for the dispersed area but can be extended to the agglomerates exhibiting much larger G^+ downshifts.

As the detailed analysis of these observations goes beyond the scope of this article, we refer to an upcoming work which will comprise a more detailed study of the D/G^+ -

Figure 4 Raman spectra of CNT agglomerate (1) and two different spots (2 and 3) in the dispersed area of composite collected at 15.6 kW/cm^2 with 2.33 eV photon excitation energy. Inset: G-band area of the spectra normalized to maximum G^+ intensity. The line drawn through G-band maxima is just guide to the eyes.

intensity ratio of both the PMMA–CNT composites and the source SWCNT material before and after functionalization [19].

4 Conclusions In summary we studied the boundary region between SWCNT aggregates and the dispersed phase of a SWCNT–PMMA composite material by Raman imaging. The width of this boundary area varies with the agglomerate size. A drop in G^+ intensity accompanied by an increase of the D/G^+ ratio was observed from aggregated to dispersed area indicating a lower CNT concentration and also that the dispersed phase contains preferentially functionalized SWCNTs. Furthermore, we observed inhomogeneities in CNT distribution even in the dispersed phase stemming from the G-band intensity difference and downshift.

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