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Quantitative description of the spatial dispersion of carbon nanotubes in polymeric matrix

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Abstract The article describes methodology for quantitative description of the dispersion of carbon nanotubes (CNT) in a nanopolymeric composite, which is based on application of scanning transmission electron microscopy combined with computer-aided image analyses. This methodology has been applied to study spatial arrangements of CNT in two polymeric resin-based composites developed for aerospace applications. The obtained quantitative characteristics of the CNT distribution are subsequently used to discuss the properties of the composites in question. In particular the electrical conductivity of the nanocomposites is analysed in terms of the critical distance between the CNT.

Introduction

Carbon nanotubes (CNT) are nowadays widely used as nanomodifiers of polymeric matrices of engineering composites developed for variety of applications (see for example EMI shielding, automotive materials, photovoltaic, packaging [1, 2]). They are used in particular for modifications of the composites used in aerospace structures, which in addition to light weight should exhibit relatively high electrical conductivity. Beneficial effects of CNT supplement have been reported for such polymeric media as epoxy, polyurethane, PMMA [3–6]. However, it is well-known that these effects are observed if the CNT are properly dispersed in the volume of the composite in question. In this context, a number of methods have been reported which improve dispersion of CNT, such as special mechanical mixing, calandering, extrusion and ultrasonic activation or combination of these methods [3, 7, 8], which can be further facilitated by functionalising their surface [9–12].

Despite a great interest in CNT composites, development in this field is far from satisfactory. This is to a considerable degree due to difficulty in direct control of the dispersion of CNT in the volume of composites. This difficulty is related to: (a) their small size, which requires for CNT imaging application of high magnification microscopic techniques, such electron and atomic force, and (b) the fact that their properties are far different from those of the polymeric matrices, which make preparation of the samples for observations of CNT dispersion quite challenging. In this situation dispersion of CNT is frequently evaluated in an indirect way, via measurements of dispersion sensitive properties. Such indirect methods impose considerable constraints on the interpretation of the data, in particular in the case of electrical conductivity, which changes drastically, over a few orders of magnitude, with addition of up to 0.5 vol.% of CNT. With such a small volume fraction even well-dispersed CNT remain isolated by the matrix and the question arises what is the critical distance between them, below which good macroscopic electrical conductivity is achieved.

In the present study we performed direct observation of CNT and examined quantitatively their dispersion in nanocomposites with polymeric matrix. The methodology used to this end is based on imaging of CNT with scanning transmission electron microscopy, STEM, and computer-aided image analyses of the representative images. The results of the quantification presented here are used to explain properties of the nanocomposites developed in this

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study. Particular attention is paid to the electrical conductivity and its relationship to the distribution function of the distance between the CNT.

Experimental

Two types of CNT-modified composites were investigated in the present study. Both composites were based on the same resin Araldite LY 1564 + XB3487.

Series A of the composite samples contained 0.5 wt% of non-modified CNT supplied by Nano-Partner-Leszek. The tubes have been mixed with the polymeric resin with addition of 0.1 wt% of surfactant BYK-9076 (BYK-chemie GmbH) and mechanically mixed at 50 °C under 2000 rpm for 15 min. Next ultrasound activation has been applied for 20 min in 30 s intervals.

Series B samples contained the same density of CNT modified with NH_2 groups. These samples were first mixed under the activation of ultrasounds for 0.5 h in ethanol, next mechanically with the addition of epoxy resin for 1 h. Finally ultrasound activation has been applied for 1 h.

For both kind of nanocomposites curing agent was added after ultrasonification, and mixed with epoxy resin containing nanotubes. All samples, series A and B have been cured at 60 °C and subsequently 120 °C, for 4 h at each curing temperature.

The structures of the fabricated nanocomposite have been investigated on sections cut with Leica EM UC6 Ultramicrotome using Atomic Force Microscopy, AFM, manufactured by Veeco and STEM by Hitachi.

Representative images obtained in STEM observations are shown in Fig. 1a and b for composite series A and B, respectively. It can be noted that the images obtained via STEM well meet criteria of computerised analysis, with individual CNT in a useful contrast against the background of the polymeric matrix. STEM images of the nanocomposite structure have been transformed into digital and analysed using methods of image analyses. In particular, the imaged positions of CNT have been used to define so-called Zones of Influence, ZI, by SKIZ method (see for example [13]), as shown in Fig. 1c–f.

The average size of the Zones is a function of the aerial density of the CNT. On the other hand coefficient of variation of the size of these regions, defined as the standard deviation divided by the average value, is a measure of uniformity in spatial distribution (dispersion) of CNT. This coefficient is equal to zero, $CV = 0$, for CNT evenly spaced on the section of the composite. It increases with the increasing non-homogeneity of their distribution with the rate which depends on the tendency for clustering.

The frequency distribution functions of the two parameters have been used to size the Zone of Influence: area A and equivalent diameter, d. Values of these parameters have been determined for randomly selected fields of observations containing in over 300 CNT each. The mean values and coefficients of variation of A and d measured for all fields of observations have been collated into a global analysis for the two series of the composites fabricated in this study.

The quantitative description of the spatial distribution of CNT

The results of the global analyses of the size of ZI are shown in Fig. 2a and b for the series A and B, respectively. It has been found that the average value of the equivalent diameter, $E(d)$, and of the ZI area, $E(A)$ can be estimated for nanocomposite Series A as:

$$E_A(d) = 0.67\ \mu m$$

$$E_A(A) = 1.48\ \mu m^2$$

The values of the same parameters for the composites series B are:

$$E_B(d) = 0.58\ \mu m$$

$$E_B(A) = 1.48\ \mu m^2$$

The average values of the ZI area can be directly used to estimate aerial density of CNT, N_a, which is equal to 17.66 and 17.58 $1/\mu m^2$ for Series A and B, respectively.

The histograms for the experimental distributions of equivalent diameter and area of the Zones of Influence are shown in Fig. 2a and b. These histograms are plotted using a logarithmic scale, which transform log-normal distributions into normal ones. To a first approximation the histograms obtained for the types of composites look quite analogous and similar to log-normal distribution. A more closer examinations of the histograms presented in Fig. 2 reveal, however, that they differ in the distribution of Zone of Influence for the composites of the series B is somewhat skewed. The coefficients of variation for equivalent diameters, d, for the B series has been estimated at $CV_B(d)=0.58$ and for A series, $CV_A(d)=0.67$. This can be interpreted as an indication of a higher uniformity of the dispersion of CNT in nanocomposites series B, which were prepared using ethanol as a solvent.

It should be also noted that the distribution function of the ZI size are relatively wide. Although the most frequent values of the equivalent diameter of the Zones are in the range 100–150 nm, for the series A and B, the largest Zones exceed 1 μm in size. This implies that some of CNT in the composites are separated from the nearest neighbours by a mantle of the thickness exceeding 500 nm. Such a separation is fully acceptable from the point of view of

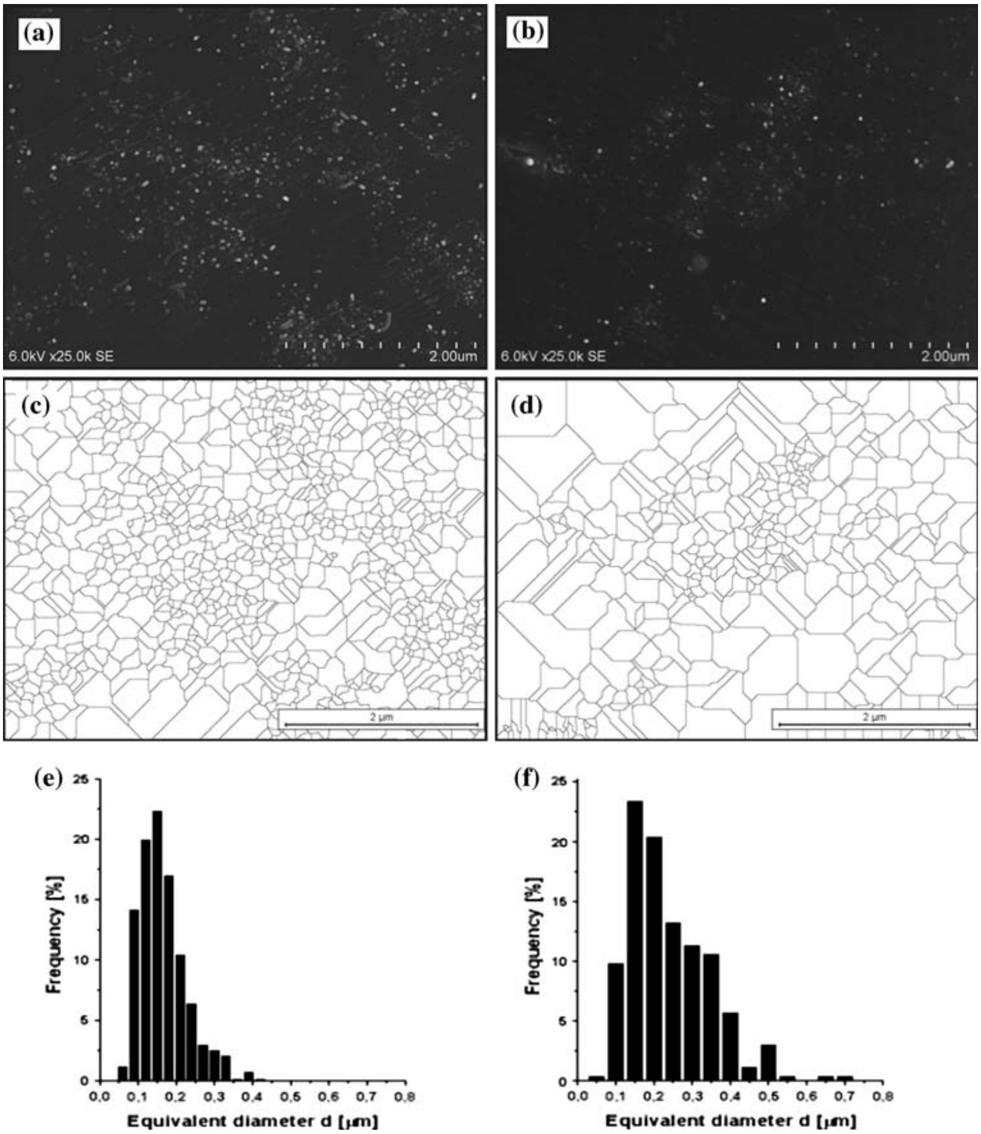

Fig. 1 STEM images obtained for a cross-section of the composites: **a** series A; **b** series B; **c** Zones of Influence for image in **a**; **d** Zones of Influence for image in **b**; **e** histogram of the ZI area for image in **c**; **f** histogram of the ZI area for image in **d**

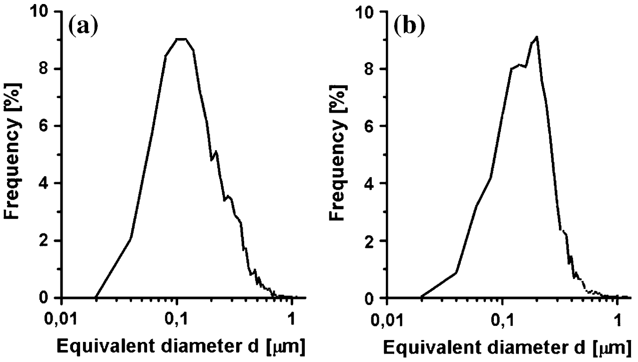

Fig. 2 Histogram of the global frequency of the appearance of the ZI equivalent for the composite series: **a** A and **b** B

the improvement in mechanical properties (e.g. hardness), which in the case of the polymeric matrices, to a first approximation does not depend on the distance between the strengthening particles. On the other hand it may have a detrimental effect on the electrical conductivity, which is controlled by short paths between the highly conductive CNT. This, however, is discussed in more details in the further text.

The properties

The properties measured in the present study included hardness, bending and tensile strengths, impact resistance and electrical resistivity. The surface and volumetric conductivity were measured using DC voltage source Model 8009 Keithley Resistivity Tester according to ASTM D-257 “Standard test methods for dc resistance or conductance of insulating materials”. Hardness was measured by the Shore D method according to PN-EN ISO 868:2005

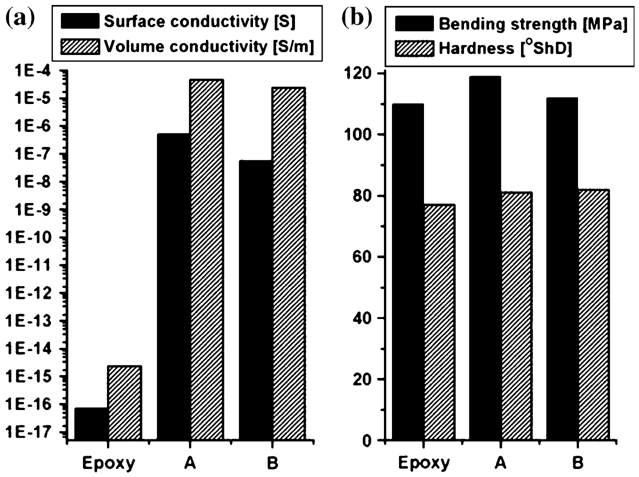

Fig. 3 Properties of the epoxy resin and composites series A and B: **a** surface and volume conductivity; **b** hardness and bending strength

and bending strength using MTS Q/Test 10 machine according to PN-EN ISO 178:2006.

Some of the results obtained in the measurements of mechanical and electrical properties are shown in Fig. 3. It can be noted from the data presented in these figures that slightly higher uniformity of the dispersion of CNT in composite series B has no much effect on the electrical conductivity and properties, although it seems to correlate with a slightly higher hardness of the samples of series B.

Discussion

The results obtained in the present work confirm already well-proven observation that addition of c.a. 0.5 wt% of CNT has a profound impact on the electrical conductivity of the resin matrix composites, which increases by approximately 9 orders of magnitude, from less than 10^{-13} to 10^{-4} [S/m]. It should be noted that similar conductivity has been reported for a number of composites with such a concentration of CNT, as reviewed in Ref. [3].

The rapid increase in the conductivity of the composites containing only 0.5 wt% of CNT, which account for approximately 0.5 vol.% is in contrast to the microstructure observation which show that the some CNT remain in a considerable distance, exceeding 500 nm. On the other hand, electrical conductivity of such a system is controlled not by average distance between the CNT but by shortest paths through the structure. In fact, spectacular changes in the conductivity of CNT-modified resins are modelled in terms of the localised transport phenomena using the theory of percolation. According to this theory (see for example [14]) the conductivity is proportional to $\left(V_{\mathrm{V}} - V_{\mathrm{V}}^{\mathrm{c}}\right)$, where: V_{V} is the volume fraction of CNT, $V_{\mathrm{V}}^{\mathrm{c}}$ is the critical volume for which the CNT form percolated structure and t is the critical exponent for conductivity. It has been further argued, see [14], that percolated structure is formed even when the individual CNT remain in some distance, δ, which is determined by fluctuations induced tunnelling. The literature data suggests that for polymeric matrices this distance may range from a few to several hundreds of nanometres [15–17].

It should be noted in this context, that the present data quite directly described relative positions of the CNT which can be used estimate the values of δ in the nanocomposites investigated in this study. Such an estimation, however, requires finding the shortest connections between the individual CNT. To this end we use here mathematical morphology in the way, which is explained below.

Binary images representative of the microstructures of CNT-modified composites have been subjected to the operation called dilatation. This operation, carried out with a specific dilatation distance, d, changes each CNT into bigger one, of the diameter extended by d. As a result, CNT which stay in the distance smaller than d come into contact and are treated in the further step as one particle. As a result, the transformed images are characterised by progressively higher area fraction and progressively smaller number of the “particles” into which are converted the CNT revealed on the sections of nanocomposites.

The above described operations of dilatation, illustrated by a series of binary images shown in Fig. 4, have been performed for different values of d. The resulting structures, which illustrate the connectivity between the CNT have been analysed in terms of the critical distance δ. It has been assumed that this distance, δ, can be inferred from the plots of the relative number of particles (per unit area) obtained by dilatation of CNT revealed on sections of the nanocomposites studied here.

The results of measurements of the number of particles against the dilatation distance are shown in Fig. 4b and c. It can be noted that the relative numbers of the CNT-based enlarged particles drops rapidly with d values increasing from 0 to approximately 150 nm. In fact, an increase of d from 0 to 0.2 results in a decrease in the number of individual CNT-based “particles” by two orders of magnitude. Also, it can be noted that saturation level is reached at around d equal to 0.2. This is a clear indication that in the present study, the δ value can be approximated in a conservative way by $d = 200$ nm. On the other hand, already for d=100 nm, more than 90% of the CNT become connected to their nearest neighbours. Both values are in agreement with some literature data—see for example [3]. Their physical interpretation is a subject of a separate research carried out currently by the Authors.

The results shown in Fig. 4b and c indicate that the differences in the spatial arrangements of CNT in the

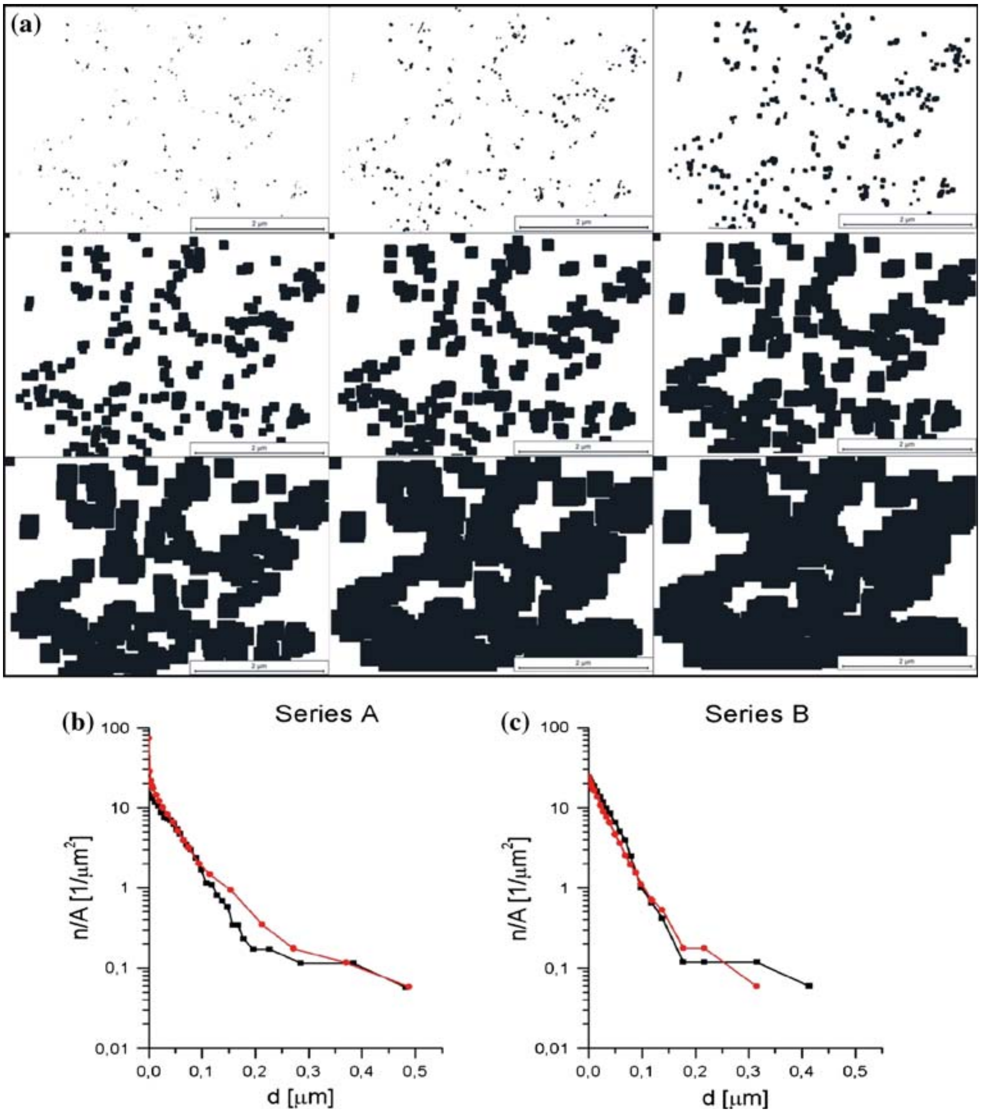

Fig. 4 Sequence of images obtained via dilatation of an image recorded in UHRSEM observations (**a**) and the variation in relative number of dilated CNT as function of dilatation increment *d* (**b**) and **c** for two fields of observations in the composites series A and B, respectively

composites series A and B are rather small and that for the latter, composites series B, the critical distance δ is smaller. On the other hand, conductivity of series B composites is lower. This indicates that ethanol used as a solvent may have detrimental effect on the conductivity of the CNT–resin matrix composites.

Conclusions

The following conclusions can be drawn the results presented here. First, modern microscopic techniques, combined with the image analysis, can be used for direct observations/quantifications of the dispersion of CNT in polymeric matrices. Second, the quantitative description of the spatial arrangement of the CNT can be extended to analyse the critical distance between the CNT which assures high conductivity of the polymeric matrix composites. The results reported here suggest also that this critical distance is in the range of 100–150 nm. A spatial distribution of CNT meeting this criterion can be obtained in polymeric matrices with standard methods of mixing and their functionalising.

Finally, it should be noted that numerical results discussed here are specific to the composites fabricated in the present study. On the other hand, the methodology proposed is of general character and may provide better insight into electrical properties of CNT composites obtained also in different technological regimes. On the other hand, it should be noted that the estimation of the critical distance between the CNT given here agrees well with the data reported in the literature (e.g. [14–17]). A semi-universal character of the estimate obtained here is to some degree supported also by the fact that threshold value of the CNT volume fraction changes in relatively narrow range from 0.2 to 0.5 vol.%.

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