# Synergistic effects in network formation and electrical properties of hybrid epoxy nanocomposites containing multi-wall carbon nanotubes and carbon black

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**Abstract** Epoxy nanocomposites including multi-wall carbon nanotubes (MWCNT) and carbon black (CB) were produced and investigated by means of electrical conductivity measurements and microscopical analysis. Varying the weight fraction of the nanoparticles, electrical percolation behaviour was studied. Due to synergistic effects in network formation and in charge transport the inclusion of both MWCNT and CB in the epoxy matrix leads to an identical electrical behaviour of this ternary nanocomposite system compared to the binary MWCNT-epoxy system. For both types of nanocomposites an electrical percolation threshold of around 0.025 wt% and 0.03 wt% was observed. Conversely, the binary CB nanocomposites exhibit a three-times higher percolation threshold of about 0.085 wt%. The difference between the binary MWCNT-epoxy and the ternary CB/MWCNT-epoxy in electrical conductivity at high filler concentrations (e.g. 0.5 wt%) turns out to be less than expected. Thus, a considerable amount of MWCNTs can be replaced by CB without changing the electrical properties.

## Introduction

The excellent conductivity of carbon-based nanoparticles makes them suitable to impart electrical conductivity to polymers [1–3]. The most widely used type of carbon nanoparticle so far is high conductive carbon black (CB),

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already used in numerous industrial applications. Their electrical behaviour in polymer systems has been extensively studied [4–7]. Although some earlier works [8, 9] report about the existence of carbon nanotubes (CNT), Iijima [10] was the first who systematically described CNT in 1991. Since then, extensive work was done in the field of CNT-modified polymers [11–23]. Their high aspect ratio as well as morphological differences compared to CB result in a reduction in percolation threshold (critical filler concentration for insulator/conductor transition) of up to one order of magnitude in polymer systems [15]. Additionally, the maximum electrical conductivity can be increased using CNT instead of CB [15]. In case of thermoset matrices, such as the one used in this work, the electrical conductivity is mainly controlled by the initial dispersion of carbon nanoparticles followed by reagglomeration process during curing [12, 18]. Among others, the parameters controlling the percolation are the geometrical dimensions of the particles, their interactions with the constituents of the epoxy matrix (i.e. zeta-potential), interparticle interactions and, in case of fibrous particles, entanglements.

In this study, we compare the potential of CB and multi-wall carbon nanotubes (MWCNT) as conductive fillers in an anhydride cured epoxy system. Additionally, we describe a new approach for improved electrical properties in an epoxy matrix by using CB and MWCNT simultaneously, leading to a ternary system. The formation of a hybrid structure between both types of particles leads to synergistic effects in network formation. In literature, only few works were done dealing with multiphase nanocomposites. For example, it is reported that the combination of CB and nanoclay in polyamide can cause an altered state of dispersion, inducing changes in the electrical percolation behaviour [24]. Liu and Grunlan [25] found a decreasing percolation threshold with the addition of nanoclay to

single-wall carbon nanotube epoxy composites. Similar results were found in previous studies for carbon nanofibre/nanoclay-epoxy composites [26]. Increased electrical conductivities were also found in epoxy nanocomposites by using CB and silica [27] or MWCNT and graphite nanoplatelets [28]. In contrast, earlier works of our group report decreasing electrical conductivities if titania nanoparticles are added to MWCNT epoxy systems [29].

When blending two conductive fillers in a polymer matrix, it is likely that co-supporting networks of both fillers form out leading to improved electrical conductivity of the polymer systems [28, 30]. In addition to that, Sun et al. [31] found synergistic effects for mixed CB/MWCNT filled polymers. They also extended the excluded volume approach in percolation theory for three phase systems, which will be used in this study to discuss the synergistic effects in CB/MWCNT-epoxy systems.

## Experimental

The epoxy system consists of a DGEBA-based resin (LY556), an anhydride curing agent (CH917) and an amine-based accelerator (DY070), provided by Huntsman, Switzerland. The resin system provides good mechanical and thermal properties and is certificated for aeronautic applications. The carbon black (Printex XE2) consists of spherical nanoparticles with a primary particle size of 30 nm, provided by Degussa-Evonik, Germany. The multi-wall carbon nanotubes (Graphistrength C100) exhibit an outer diameter of about 15 nm with length of up to 10 μm, and were provided by Arkema, France.

The nanocomposites were produced using a high shear mixing process including a lab-scale three-roll-mill (Exakt 120E). First, the nanoparticles were manually stirred in the resin. The pre-dispersed suspension was then given batchwise onto the rolls with dwell times of 2 min. The final dispersion takes place between the rolls of the three-roll-mill. The gap between the rolls of 5-μm leads to very high shear forces throughout the whole volume of the resin which cause a superior state of dispersion for the nanoparticles. Details about the dispersion technique can be found in earlier publications [32, 33]. After dispersion of the nanoparticles in the resin, the hardener and accelerator are added in a vacuum dissolver in order to avoid trapped air in the suspension as described in [34]. The filler concentration was varied in small steps from very low (0.0025 wt%) to high (0.6 wt%) weight content. In the ternary systems, the ratio between CB and MWCNT were set to 1:1, e.g. 0.2 wt% CB plus 0.2 wt% MWCNT.

The uncured samples were poured into an aluminium mould ($100 \times 180$ mm$^2$) and cured in an oven following the recommended curing cycle (4 h at 80 °C plus 8 h at 140 °C). After curing, samples for impedance spectroscopy were machined from the middle part of the sample. For each filler content four samples were cut to a geometry of $10 \times 10 \times 1$ mm$^3$. The surfaces were covered with conductive silver paint. In order to obtain information about the dispersion in the cured state, the AC electrical conductivity was measured in the frequency range between 20 Hz and 1 MHz with a HP4826 impedance analyzer. The electrical conductivity values used in the percolation diagrams were taken at 1 kHz. According to earlier publications, AC conductivity at low frequency can be correlated with DC conductivities. Furthermore, at low frequency the capacitive part of the AC conductivity can be neglected. Transmission electron micrographs were taken using a Philips EM 400 at 120 kV. Ultra thin films of the nanocomposites (w = 50 nm) were obtained by ultramicrotome cutting. Transmission light micrographs were taken using a standard light microscope. Samples were prepared from conductivity samples by grinding down to 0.2 mm with additional polishing.

## Results and discussion

Figure 1 shows the electrical conductivity of the two binary as well as of the ternary nanoparticles epoxies as a function of filler content. As expected, the binary CB-epoxy systems (grey triangles) exhibit a higher percolation threshold than the binary MWCNT-epoxy systems (open squares). Additionally, the electrical conductivities at high filler contents tend to be much higher for the MWCNT systems, up to two orders of magnitude.
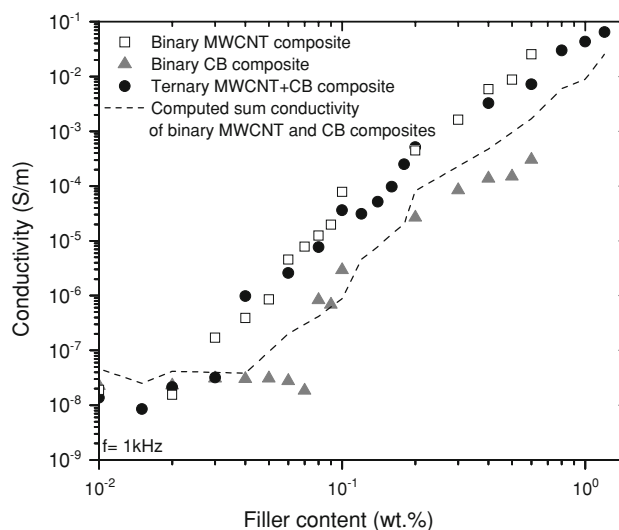


Fig. 1 Electrical conductivity for the produced nanocomposites exhibiting percolation behaviour

The ternary system (CB and MWCNT) exhibits almost the same electrical behaviour as the binary MWCNT-epoxy. The percolation threshold seems to be almost identical and the conductivity at high filler contents is slightly lower. Since the half amount of the included filler consists of CB this behaviour is unexpected so far. In order to point out this phenomenon, the conductivities of the binary systems were summed up (dashed line). Although the electrical conductivity is not linearly dependent on the filler content the sum curve gives an estimation of the electrical behaviour of the blended ternary system assuming no synergistic effects. Thus, the difference between the computed sum curve and the experimental curve gives evidence for the presence of synergistic effects in ternary systems.

In order to perform a deeper analysis, the data of the three systems was fitted according to the classical percolation scaling law [35, 36]:

$$\sigma = \sigma_0(\Phi - \Phi_c)^t \tag{1}$$

where $\Phi$ is the filler content and $\Phi_c$ the percolation threshold, $\sigma_0$ the conductivity at $\Phi_c$ and $t$ the percolation exponent.

According to [36] the percolation threshold in the fitting was changed incrementally in small steps ($\Delta\Phi = 0.001$ wt%) in order to obtain a best fit of the experimental data, as it can be seen in Fig. 2. The percolation threshold for the CB-epoxy is at 0.085 wt%. The MWCNT-epoxy system exhibits a three times lower percolation threshold of about 0.025 wt%. As mentioned above, the ternary system provides almost the same percolation threshold as the binary MWCNT-epoxy (0.03 wt%). The difference between the CB- and the MWCNT-epoxy is reported to be much higher (up to one order of magnitude) in other epoxy

systems based on an amine hardener [33]. The relative difference of acitity/basicity for CB and amine groups leads to a negative surface charge of the CB [37]. In contrast, the used anhydride system is less basic. This impedes less negative surface charge due to a different zeta-potential for the carbon nanoparticles [6]. Thus, reagglomeration processes are promoted leading to a rather small change in percolation threshold compared to the system presented in [33].

The binary MWCNT-epoxy and the ternary CB/MWCNT-epoxy posses similar percolation exponents with values of $t = 3$ and $t = 2.85$, respectively. A significant lower exponent was found for the CB-epoxy system with $t = 1.27$. From theory, the percolation exponent $t$ reflects the dimensionality of the system. Values from 1 to 2 reflect two and three dimensional systems. Values around three were found for systems based on a Bethe-lattice [11]. It has to be denoted that Eq. (1) is derived from statistical percolation theory and is only valid for filler contents above the critical filler content $\Phi_c$. Since the percolation in filled epoxy systems is based on dynamic mechanisms, mostly taking place during curing, the fitted curve in Fig. 2 can only be used for a qualitative estimation of the different percolation behaviours. Thus, the values for the percolation exponent $t$ cannot be linked to a certain dimension of the microstructure. The contact resistance and tunnelling distance between the particles must also be taken into account. In review, a huge scattering in experimental results for filled polymer systems was found, leading to values mostly between 2 and 3 [11]. Nevertheless, in this study the matrix polymer, as well as the production route, is kept constant which allows a comparison among these systems. The percolation exponent $t$ is the slope of the fitted line and represents the dependence of the electrical conductivity on the filler concentration above the percolation threshold. Thus, $t$ is somehow dependent on the number and magnitude of the contact resistance between the nanoparticles. Regarding the ternary system, all three major features of the percolation curve appear to be almost identical compared to the binary MWCNT-epoxy, e.g. percolation threshold $\Phi_c$, percolation exponent $t$ and the conductivity at high filler contents.

According to [31] the percolation threshold of ternary systems can be estimated by using an equation derived from the "excluded volume" approach [38]:

$$\frac{m_{CB}}{\Phi_{CB,binary}} + \frac{m_{CNT}}{\Phi_{CNT,binary}} = 1 \tag{2}$$

where $m_{CB}$ and the $m_{CNT}$ are the mass fractions in the ternary systems, $\Phi_{CB,binary}$ and $\Phi_{CNT,binary}$ the respective percolation thresholds in the binary systems. In this study, $m_{CB}$ equals $m_{CNT}$ since the ratio of CB and MWCNT is set to 1:1. Using the percolation threshold of the binary
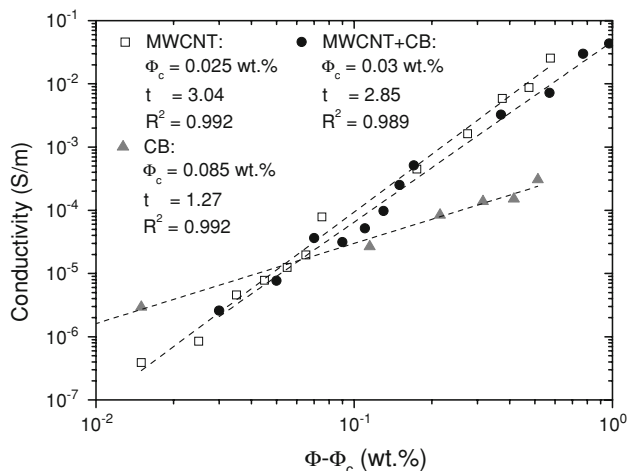


Fig. 2 Fitted percolation curves according to Eq. (1) for the produced nanocomposites

systems according to Fig. 2 it is possible to obtain the filler contents of each particle of the ternary system:

$$m_{CB} = m_{CNT} = \frac{0.085}{4.4} = 0.02 \, \text{wt\%} \qquad (3)$$

Thus, the percolation threshold of the ternary system is:

$$\Phi_{ternary} = 2m_{CB} = 2m_{CNT} = 0.04 \, \text{wt\%} \qquad (4)$$

Comparing the experimental percolation threshold (0.03 wt%) with the theoretical one (0.04 wt%), a difference can be found. Since this difference is rather small, a statement on the presence of synergistic effects in percolation dynamics in the ternary system cannot be made. Nevertheless, differences between the ternary CB/MWCNT system and expected behaviour, reflected by the sum curve in Fig. 1, are more pronounced above the percolation threshold. In order to obtain evidence of this feature, transmission electron and light microscopy were conducted on selected filler concentrations (0.04 and 0.1 wt%). According to Fig. 3, a dispersion of CB and MWCNT on the primary particle level can be found leading to co-supporting networks, which were also found for other combinations of carbon based particles [28, 31]. Assuming that different types of carbon nanoparticles posses similar surface characteristics, this allows a good intermixing of both types of particles without a formation of domains or other substructures as reported for other nanoparticle combinations [27, 39].

These co-supporting networks of CB and MWCNT (see Fig. 3b) can also be found at lower magnifications in transmission light microscopy revealing differences in the distribution of nanoparticles and their different formation of networks. In Fig. 4 images of nanocomposites containing 0.04 wt% are shown. The binary MWCNT as well as the ternary CB/MWCNT systems show a formation of networks which lead to conductivities above the percolation threshold. Although the ternary system contains of 0.02 wt% of each of the nanoparticles (0.04 wt% in total), the network structure appears to be much denser than the binary MWCNT system. The CB system does not show a comparable network structure, thus leading to conductivities below percolation.

An analogue behaviour was also found for a higher filler content of 0.1 wt%. Here, the binary MWCNT system shows a denser structure than the ternary CB/MWCNT system which can be explained in terms of a lower filler content of MWCNT in the ternary system. This is also reflected in the corresponding conductivity values which are slightly lower than the binary MWCNT system. Regarding the 0.1 wt% CB system, again a low pronounced network was found. From the findings in electrical percolation behaviour as well as the revealed microstructures it can be concluded that synergistic effects must have occurred. These effects are more reflected in the electrical
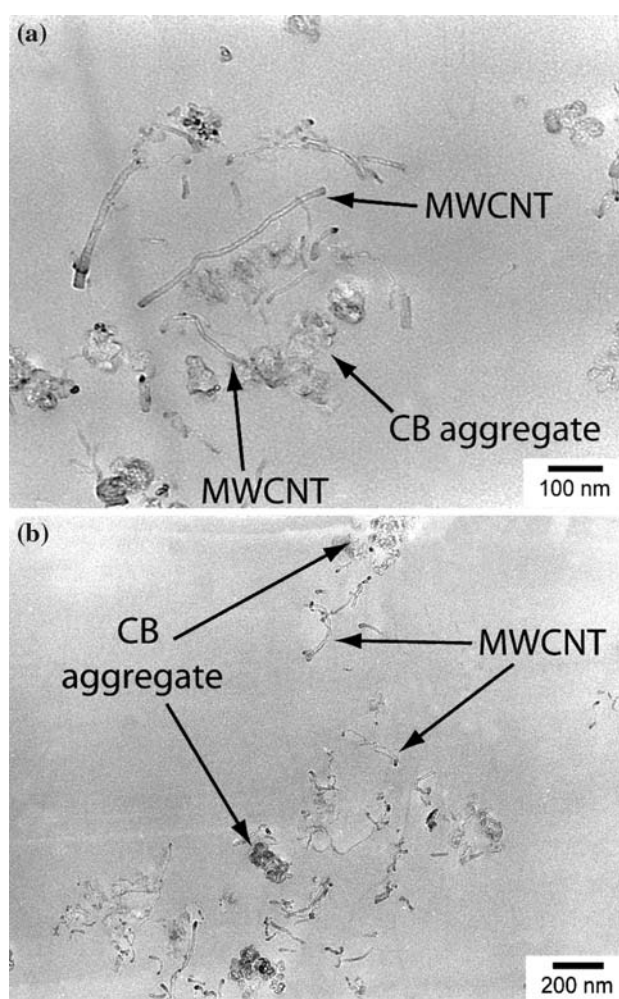


Fig. 3 TEM-images of a ternary CB/MWCNT (0.2/0.2 wt%) nanocomposite showing **a** primary particle dispersion and CB/MWCNT contacts (mag. 60,000×), **b** co-continuous network formation of CB and MWCNT (mag. 28,000×)

conductivities at high filler contents rather than in the percolation threshold.

It is obvious that CB itself can also reagglomerate, which causes the presence of a dynamic percolation threshold in binary CB systems. This feature can be used to explain the similar reagglomeration mechanisms of the binary MWCNT-epoxy and the ternary CB/MWCNT-epoxy. Since the differences between the experimental (0.03 wt%) and the theoretical percolation threshold (0.04 wt%) is rather small, it can be concluded that synergistic effects based on reagglomeration are negligible in case of an CB/MWCNT ratio of 1:1. Therefore it is likely that the proposed synergistic effects are mostly based on the network structure leading to identical conductivities even if half of the MWCNT content is substituted by CB. In order to understand these synergistic effects two theoretical cases are discussed in Fig. 6.

**Fig. 4** TLM-image of nanocomposites containing 0.04 wt% of nanoparticles showing the spatial distribution of agglomerates and their network formation
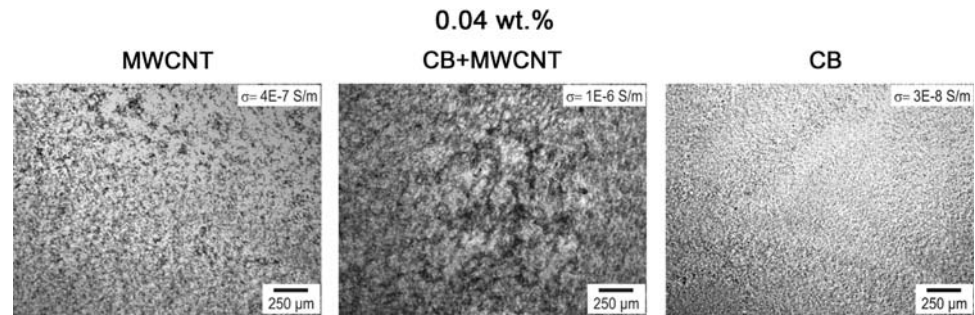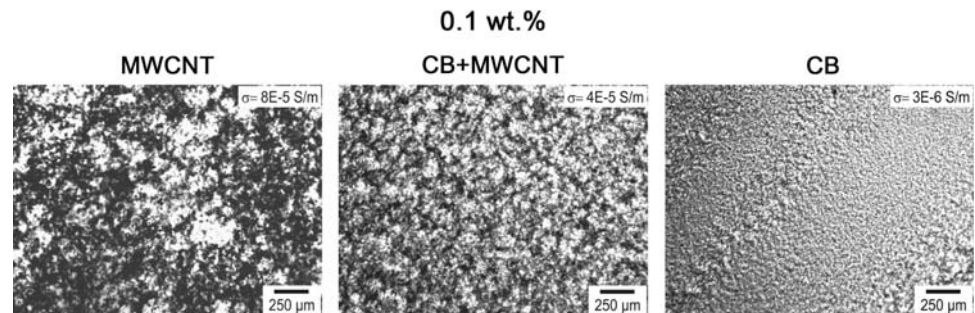


**Fig. 5** TLM-image of nanocomposites containing 0.1 wt% of nanoparticles showing the spatial distribution of agglomerates and their network formation



Case 1 regards CB as a filler, which changes the MWCNT network structure. It is known that MWCNT form a fractal type of structure which is multiple redundant, featuring branches in the network which do not contribute to the actual conductive pathway, so called "dead" branches (see Fig. 6 Case1). Thus, only a certain amount of MWCNT contributes to the charge transport. Considering now CB aggregates shortcutting some of these "dead" MWCNT branches new conductive pathways are formed. Thus, the electrical conductivity of a ternary CB/MWCNT system is higher than a binary MWCNT system.

Additionally, the tunnelling distance and the number of tunnelling contacts, which have to be overcome by charge carriers, determine the overall conductivity [40, 41]. High aspect ratio fillers as MWCNT provide a higher electrical conductivity in polymers than spherical particles as CB because their contact resistance is lower and the number is less [16, 41]. This phenomenon is reflected in the percolation exponent $t$, which is almost similar for the binary MWCNT-epoxy and ternary CB/MWCNT-epoxy. Therefore it is likely that the electron transport is mainly performed in the MWCNT network in the ternary system. In other words, the transport through MWCNT branches is facilitated by means of a lower intrinsic resistance than in the CB branches. Following this argumentation, CB can be regarded as a filler which preferable shortcuts parts of the MWCNT network rather than to build up an own network in CB/MWCNT ternary composites.

Since Figs. 3, 4 and 5 revealed co-supporting CB/MWCNT networks in ternary systems, it is more likely that CB is incorporated in conductive pathways. Our previous study showed that similar dispersion with ternary systems, including MWCNT and non-conductive titania nanoparticles, lead to decreasing conductivities by up to five orders of magnitude [29]. Conversely, the CB must be incorporated into the conductive MWCNT pathways, since conductivity is mainly preserved (see Fig. 6 Case 2). In principle, if a MWCNT is substituted by several spherical CB particles or CB aggregates increasing resistance over a certain length should be found which results in a significantly lower bulk conductivity. The reason why the experimental results and the sum curve in Fig. 1 differ significantly may be explained by the fact that the CB primary particles or CB aggregates preferably shortcut small distances of two neighbouring contact resistance points. It is obvious that the distance between two contact points in a MWCNT network is not constant and can be much shorter than an actual nanotube length.

Another reason may be found in the structural imperfection and the production process of CVD (chemical vapour deposition)-MWCNT. They posses a highly defected structure which results in curved MWCNT. The production process leads to highly entangled MWCNT. Thus, it can be assumed that the statistic length of a MWCNT–MWCNT contact must be in the length scale of a CB aggregate (few hundred nanometers). At this point we cannot finally conclude which of the two theoretical mechanisms in Case 1 and Case 2 is dominant or is present in the nanocomposite. From the findings in electrical percolation behaviour as well as the structural analysis it can be presumed that the different mechanisms occur simultaneously. Here, changing the CB to MWCNT ratio can give
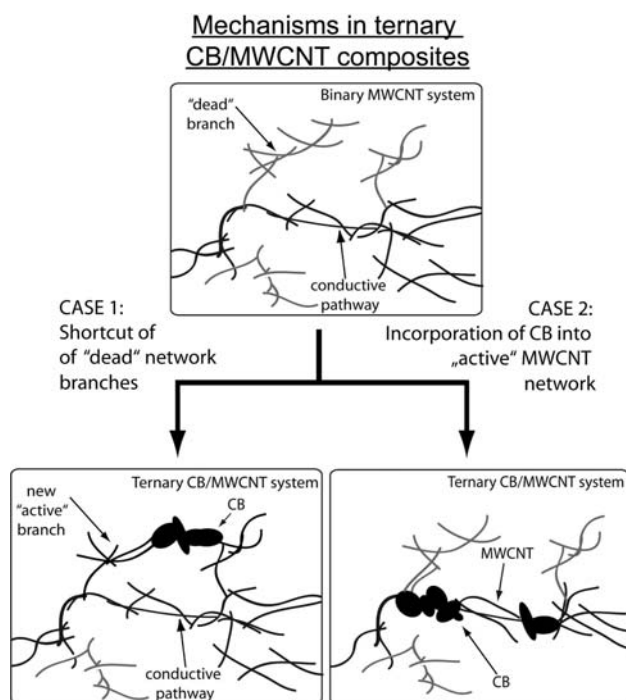
**Fig. 6** Principles of conductive pathway formation in ternary CB/MWCNT systems

further clarity about the impact of each of the mechanisms which is an object of ongoing studies in our group.

## Conclusions

The potential of CB and MWCNT as conductive fillers in an epoxy polymer was studied using impedance spectroscopy and electron microscopy. MWCNT exhibit a higher potential as functional fillers compared to CB due to their higher aspect ratio, resulting in a decreased percolation threshold and higher bulk conductivity for high filler contents. Additionally, ternary systems including CB and MWCNT were produced resulting in a hybrid structure and revealed an electrical behaviour similar to the binary MWCNT system. The percolation threshold as well as the conductivity is preserved when half of the amount of MWCNT is substituted by CB. The different behaviours of the carbon nanoparticles-modified systems were compared using percolation theory. Since the conductivities at high filler contents and the percolation exponent of the ternary CB/MWCNT-epoxy and the binary MWCNT-epoxy are similar, it is likely that MWCNT dominate the percolation dynamics and the formation of the network structure in ternary CB/MWCNT-epoxy. Besides that, CB might shortcut some parts of the MWCNT network branches. This work showed that a combination of conductive particles lead to preserved electrical properties with a

simultaneous significant reduction of the MWCNT amount. Thus, MWCNT can be substituted by a considerable amount of another type of conductive nanoparticle if the intermixing is sufficiently high and if this second type of nanoparticles possesses similar reaglomeration tendencies. As an outlook, the variation of the CB to MWCNT ratio may lead to even more improved electrical properties by adjusting an optimum microstructure.

## References

1. Thostenson ET, Li CY, Chou TW (2005) Compos Sci Technol 65:491
2. Chung DDL (2004) J Mater Sci 39:2645. doi:10.1023/B:JMSC.0000021439.18202.ea
3. Winey KI, Kashiwagi T, Mu M (2007) MRS Bull 32:348
4. Ezquerra TA, Kulescza M, Baltá-Calleja FJ (1991) Synth Met 41:915
5. Prasse T, Flandin L, Schulte K, Bauhofer W (1998) Appl Phys Lett 72:2903
6. Flandin L, Prasse T, Schueler R, Schulte K, Bauhofer W, Cavaille J-Y (1999) Phys Rev B 59:14349
7. Ezquerra TA, Connor MT, Roy S, Kulescza M, Fernandes-Nascimento J, Baltá-Calleja FJ (2001) Compos Sci Technol 61:903
8. Davis WR, Slawson RJ, Rigby GR (1953) Nature 171:756
9. Oberlin A, Endo M, Koyama T (1976) J Cryst Growth 32:335
10. Iijima S (1991) Nature 354:56
11. Bauhofer W, Kovacs JZ (2008) Compos Sci Technol (in press, corrected proof)
12. Kovacs JZ, Velagala BS, Schulte K, Bauhofer W (2007) Compos Sci Technol 67:922
13. Du FM, Scogna RC, Zhou W, Brand S, Fischer JE, Winey KI (2004) Macromolecules 37:9048
14. Bryning MB, Islam MF, Kikkawa JM, Yodh AG (2005) Adv Mater 17:1186
15. Gojny FH, Wichmann MHG, Fiedler B, Kinloch IA, Bauhofer W, Windle AH, Schulte K (2006) Polymer 47:2036
16. Hu N, Masuda Z, Yan C, Yamamoto G, Fukunaga H, Hashida T (2008) Nanotechnology 19:215701
17. Kodgire PV, Bhattacharyya AR, Bose S, Gupta N, Kulkarni AR, Misra A (2006) Chem Phys Lett 432:480
18. Sandler JKW, Kirk JE, Kinloch IA, Shaffer MSP, Windle AH (2003) Polymer 44:5893
19. Martin CA, Sandler JKW, Shaffer MSP, Schwarz MK, Bauhofer W, Schulte K, Windle AH (2004) Compos Sci Technol 64:2309
20. Martin CA, Sandler JKW, Windle AH, Schwarz MK, Bauhofer W, Schulte K, Shaffer MSP (2005) Polymer 46:877
21. Moisala A, Li Q, Kinloch IA, Windle AH (2006) Compos Sci Technol 66:1285
22. Tjong SC, Liang GD, Bao SP (2007) Scr Mater 57:461
23. Pötschke P, Abdel-Goad M, Alig I, Dudkin S, Lellinger D (2004) Polymer 45:8863
24. Konishi Y, Cakmak A (2006) Polymer 47:5371

25. Liu L, Grunlan JC (2007) Adv Funct Mater 2007:2343
26. Kotaki M, Wang K, Toh ML, Chen L, Wong SY, He CB (2006) Macromolecules 39:908
27. Zhang W, Blackburn RS, Dehghani-Sanij AA (2007) Scr Mater 56:581
28. Li J, Wong P, Kim JK (2008) Mater Sci Eng A 483:660
29. Sumfleth J, Almeida Prado LAS, de Sriyai M, Schulte K (2008) Polymer 49:5105
30. Bokobza L, Rahmani M, Belin C, Bruneel JL, El Bounia N (2008) J Polym Sci B Polym Phys 46:1939
31. Sun Y, Bao H, Guo Z, Yu J (2009) Macromolecules 42:459
32. Gojny FH, Wichmann MHG, Kopke U, Fiedler B, Schulte K (2004) Compos Sci Technol 64:2363
33. Gojny FH, Wichmann MHG, Fiedler B, Schulte K (2005) Compos Sci Technol 65:2300
34. Wichmann MHG, Sumfleth J, Fiedler B, Gojny FH, Schulte K (2006) Mech Compos Mater 42:395
35. Stauffer D, Aharony A (1992) Introduction to percolation theory. Taylor & Francis, London
36. Kilbride BE, Coleman JN, Fraysse J, Fournet P, Cadek M, Drury A, Hutzler S, Roth S, Blau WJ (2002) J Appl Phys 92:4024
37. Prasse T, Schwarz MK, Schulte K, Bauhofer W (2001) Colloid Surf A 189:183
38. Balberg I, Anderson CH, Alexander S, Wagner N (1984) Phys Rev B 30:3933
39. Sumfleth J, Prado LASA, Richau S, Sriyai M, Schulte K (2009) Solid State Phenom 151:176
40. Sheng P, Sichel EK, Gittleman JI (1978) Phys Rev Lett 40:1197
41. Li C, Thostenson ET, Chou TW (2007) Appl Phys Lett 91: 223114