Influence of Mixing Conditions on Carbon Nanotube Shortening and Curling in Polycarbonate Composites

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Abstract. Polycarbonate composites containing multiwalled carbon nanotubes (MWCNTs, 0.2-2.0 wt%) were melt mixed in small scale at different conditions of screw speed and mixing time to vary the specific mechanical energy (SME) input between 0.4 and 4.0 kWh/kg. Next to the electrical properties of compression molded plates and the MWCNT macrodispersion also the nanotube length and shape were analyzed. For this, the matrix of the composites with 0.75 wt% MWCNT loading was dissolved and the remaining nanotubes were investigated using TEM. It was found that with increasing SME input the number of remaining CNT agglomerates decreases. The MWCNT length decreased from initially about 1.4 micrometers towards 350 nanometers at a SME of 4 kWh/kg and the mean curling values were also reduced. The electrical percolation threshold increases with SME from about 0.4 wt% to 0.6 wt%.

INTRODUCTION

In composites of polymers with carbon nanotubes (CNTs) the electrical percolation at low filling grades is connected with the very high aspect ratio of CNTs. For this, good dispersion of initial agglomerates into single tubes is needed as well as preserving the initial length of CNTs. Melt mixing is an effective method to disperse MWCNTs in thermoplastic matrices. Thereby, the melt mixing conditions influence the state of dispersion significantly. Based on the steps of dispersion of primary agglomerates of MWCNTs, the melt viscosity (related to mixing temperature and shear) influences e.g. the infiltration step of polymer chains into the agglomerate structures but also the shear stresses applied on such infiltrated agglomerates in the following steps of rupture and erosion [1]. Whereas low viscosity is favorable for the infiltration step, higher viscosity favors the dispersion steps. Mixing time also plays an important role on all mechanisms involved in agglomerate dispersion. In general it was found that a higher specific mechanical energy (SME) input, achieved e.g. using higher screw speed or lower temperature (or in discontinuous mixing by longer mixing time) results in better dispersion [1-3]. On the other hand, a higher SME was also found to shorten the CNTs to higher extent [3]. As low electrical percolation threshold as well as high mechanical properties requires both, good dispersion and high retained CNT length, optimization of processing conditions is needed.

In this study, polycarbonate/MWCNT composites were melt mixed in a small-scale microcompounder by varying the mixing conditions. The electrical properties and the CNT macrodispersion were studied depending on the mixing conditions by varying the CNT content. In addition, the CNT length distribution and the curling of nanotubes dissolved from the composites were examined to judge to which extent the initial length could be retained.

EXPERIMENTAL

Composites of polycarbonate (PC, Makrolon® 2600, Bayer MaterialScience AG) and 0.25-2.0 wt% MWCNTs (Nanocyl™ NC7000, carbon purity 95%) were melt mixed at 280°C in a conical twin-screw microcompounder Xplore DSM15 by varying the mixing time (5 min, 15 min) and rotation speed (100 rpm, 250 rpm).

The specific mechanical energy (SME) input was calculated according to [2]. Electrical measurements were done on pressed plates (ø 60 mm, thickness 0.5 mm, pressing conditions: 280°C, 1 min, hot press PW40EH). For resistivities $>10^7$ Ohm cm the Keithley test fixture 8009 and for conductive samples a 4-point test fixture with gold electrodes (using strips cut from the plates) combined with a Keithley electrometer E6517A were applied. The study of CNT macrodispersion using light microscopy (LM) was performed on thin sections (10 µm) cut from the extruded strands at room temperature by a diamond knife. The quantification was done by calculation of the agglomerate area ratio A_A (%) by division of the area of agglomerates A by the area of the complete image A_0 [4].

For the determination of CNT length distribution and CNT curling the composites containing 0.75 wt% CNT were dissolved in chloroform, a drop of this dispersion was put on a carbon covered TEM grid and the single tubes were imaged by transmission electron microscopy (TEM) using a methodology described in [5]. The curling value was defined as the ratio of the total and the effective length of a single CNT (diagonal of the rectangular area which encased the CNT) as shown exemplarily in Fig. 1 (right).

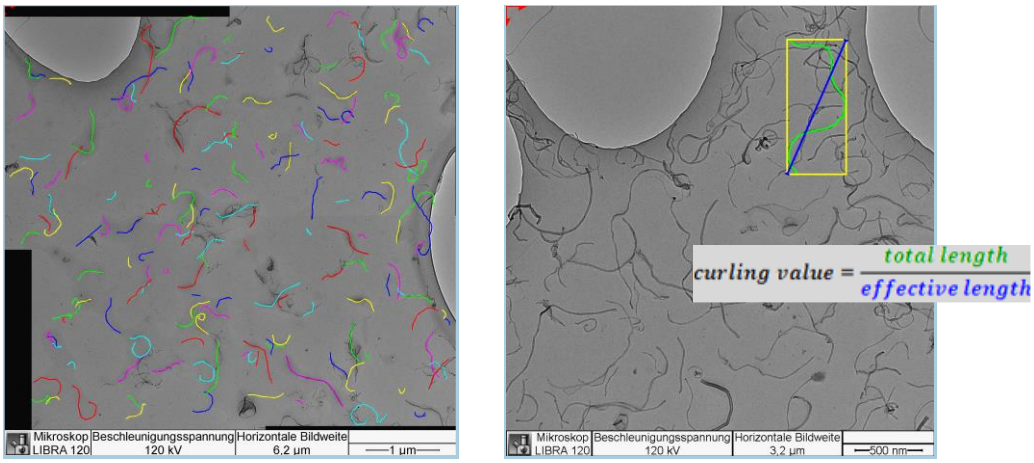

FIGURE 1. Typical TEM images with marked nanotubes (left) and the definition of the curling value (right)

RESULTS AND DISCUSSION

When varying the melt mixing conditions, the MWCNT macrodispersion was influenced as illustrated on LM images of composites containing 0.75 wt% CNTs as shown ín Fig. 2.

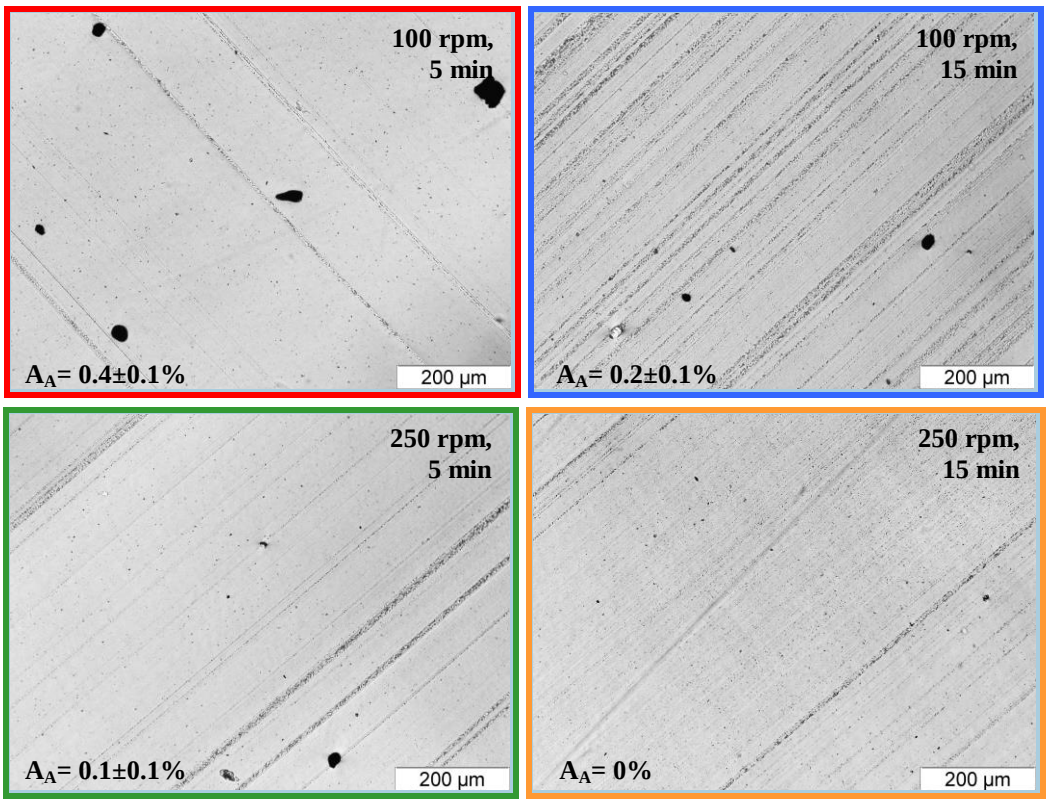

FIGURE 2. Light microscopy images and agglomerate area ratio A_A of PC/0.75 wt% MWCNT composites prepared at different mixing conditions

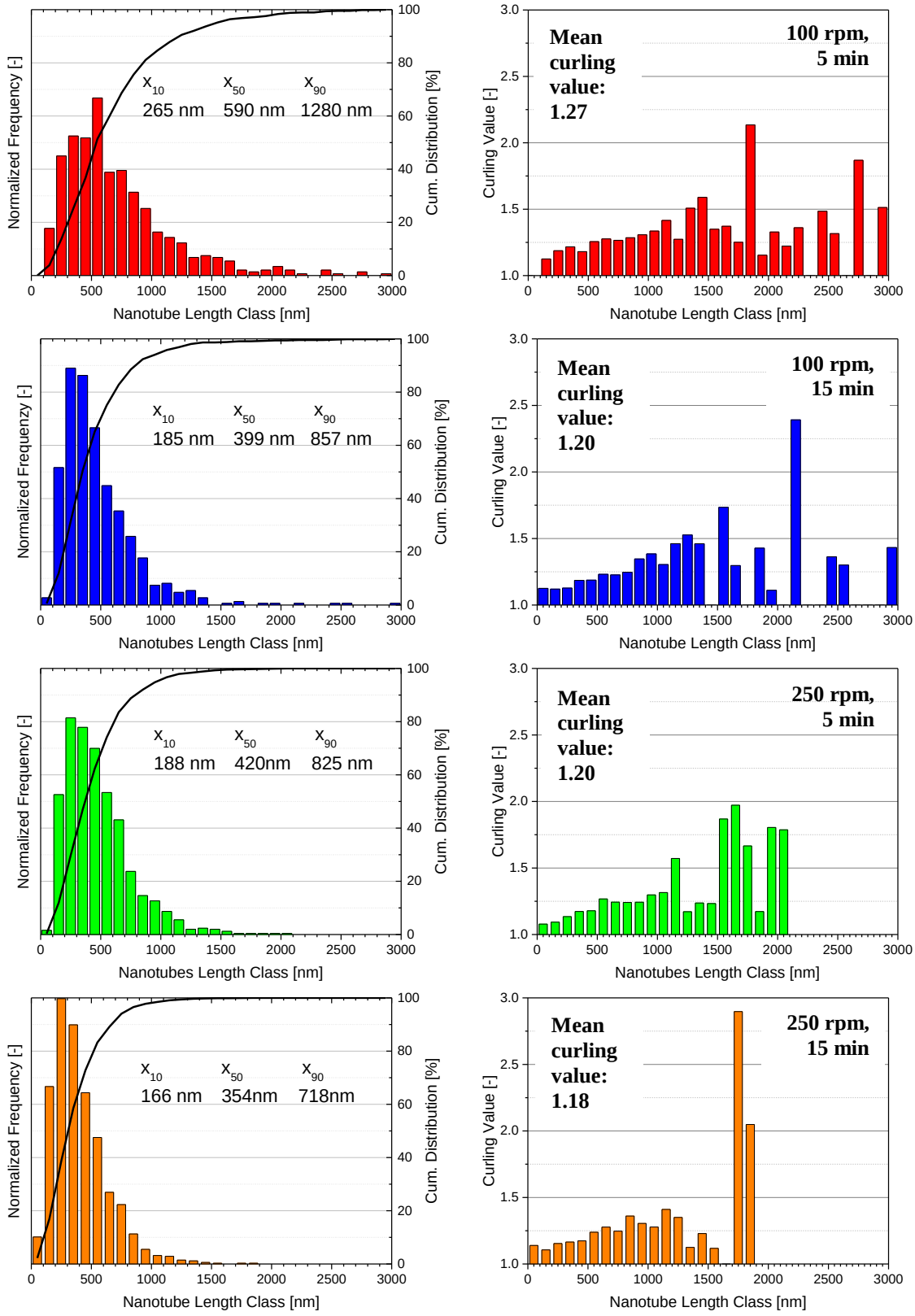

FIGURE 3. Distributions of CNT length (left column) and curling value (right column) for nanotubes extracted from the PC/0.75 wt% CNT composite prepared at 280°C and different conditions

Increasing SME input, achieved either by increased rotation speed or mixing time improved the state of dispersion as indicated by the decrease of agglomerate area ratio A_A. Agglomerate free composites could be prepared at the highest SME, based on higher rotation speed (250 rpm) and longer mixing time (15 min).

Additionally, a decrease of the MWCNT length after melt mixing could be measured. From the initial mean MWCNT length x_{50} of 1341 nm [5] the MWCNT length in the composites was reduced to values between 590 nm and 354 nm whereas the shortening was more pronounced at higher SME. The length histograms are shown in Fig. 3 (left) and the dependency of mean MWCNT length (x_{50}) on SME in Fig. 4 (top). Similar relations between SME, macrodispersion and nanotube length were described before for polycaprolactone/0.5 wt% MWCNT composites prepared using the same small-scale compounder at different rotation speeds [3]. The authors found with increasing SME (rotation speed) an improvement of the MWCNT macrodispersion with simultaneous reduction of the mean MWCNT length.

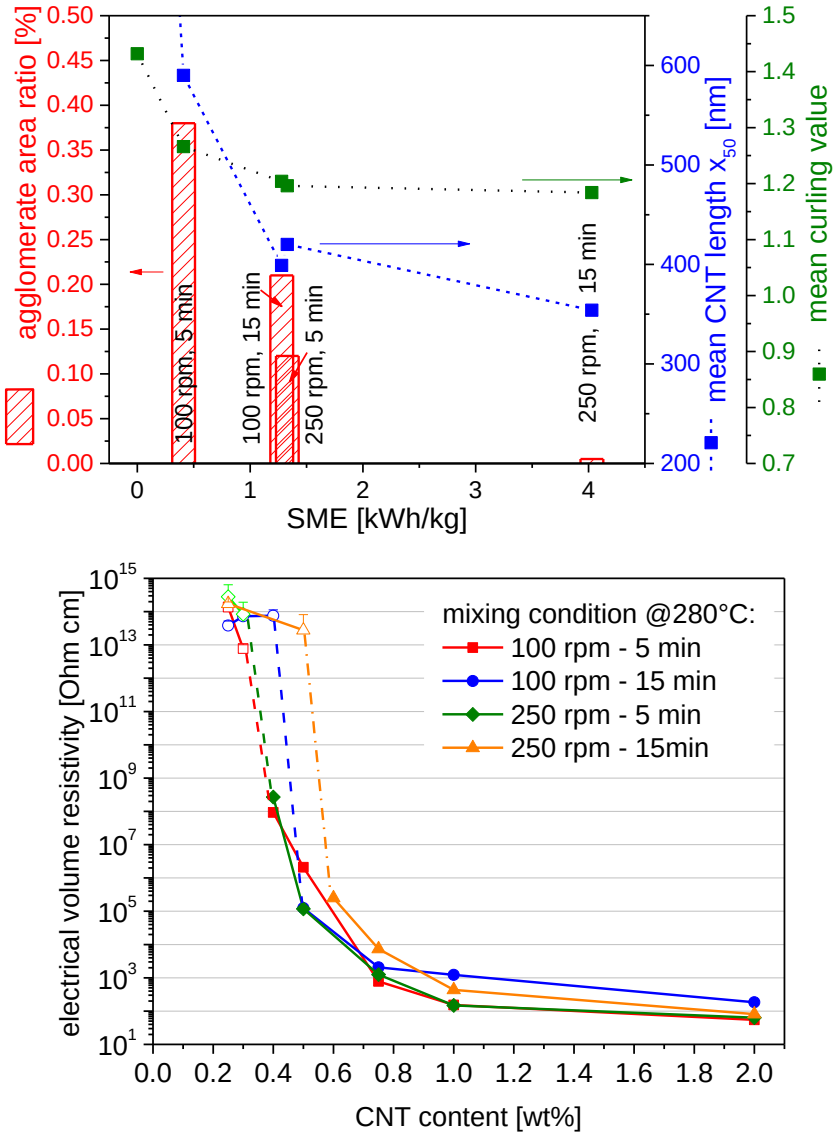

FIGURE4. Dependence of agglomerate area ratio, mean CNT length x_{50} and mean curling value on the specific mechanical energy (SME) for PC/0.75 wt% MWCNT composites prepared at different mixing conditions (top), Electrical volume resistivity versus CNT content for PC composites prepared at different mixing conditions (bottom)

Comparing the mean curling value at different mixing conditions, a decrease of the curling with increasing SME can be seen (Fig. 3 right, Fig. 4 top). Generally, the curling value lowered with decreasing MWCNT length. It can

be assumed that the nanotubes break at the defect sites and the remaining nanotube parts have a lower defect density and are straighter and more like an ideal rod shape nanotube. A lower number of defect sites in MWCNTs with lower length detected using RAMAN was described before for MWCNTs which were broken using ball milling [6].

Furthermore, the electrical percolation threshold p_c increased with increasing SME input despite better nanotube dispersion which correlates well with the more pronounced MWCNT shortening (Fig. 4 right). The values for p_c increased from ~0.4 wt% for composites prepared at 100 rpm/5 min and 250 rpm/5 min towards ~0.5 wt% for those prepared at 100 rpm/15 min and ~0.6 wt% for composites mixed at 250 rpm/15 min. When comparing the two composites with medium energy input (1.28 or 1.33 kWh/kg), interestingly, the sample with the shorter mixing time but higher speed showed slightly lower shortening and lower electrical percolation threshold. This illustrates that the mixing time seems to also be a critical factor. In addition, it shows that the combination of better dispersion and higher CNT length, as obtained at 250 rpm/ 5 min results in the lowest electrical resistivity values. The sample with best dispersion having at the same time most pronounced shortening (250 rpm /15 min) shows the highest electrical percolation.

CONCLUSIONS

When varying mixing conditions during melt mixing of PC/MWCNT composites, increasing SME input resulted in improved MWCNT macrodispersion and decreased mean MWCNT length as well as mean curling value. With decreasing MWCNT length the curling values decrease indicating that entangled nanotubes are broken into more straight parts. This is most probably due to breakage at defect sites of the nanotubes.

Electrical percolation sensitively reflects both, improved dispersion and reduced nanotube length. It seems that for electrical properties preserving the nanotube length is more critical than to obtain excellent dispersion.

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