RESEARCH ON MELT SPUN PMMA COMPOSITES WITH ALIGNED CARBON FIBERS

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Abstract

In this work, PMMA/carbon fibers (CF) composite fibers with highly oriented CFs were melt spun. The concentration of CFs was up to 56 vol. %. Both the surface and the cross-section of the composite fibers were investigated. The length of CFs from composite with different concentration of CFs was determined. The conductivity of composite fibers under room temperature was tested. The percolation threshold of the composite fibers was estimated between 23.96 vol. % and 28.64 vol. %.

1. Introduction

Chopped carbon fibers (CF) have been widely used as conductive fillers for the composites [1-3]. The conductive CFs can form a network inside the composite, which ensure the electrical current to pass. If the conductive pathway can be formed or not, depends on the concentration of the CFs. A critical value of this concentration (percolation threshold) should be reached, above which the conductivity of the composites increases significantly [4]. When the concentration of CFs below the percolation threshold, the CFs cannot contact with each other, or the number of contacted CFs is not enough for a pathway through the whole system, which means the conductivity of composite is almost like the conductivity of the polymer matrix, i.e. nonconductive. Therefore, for composites with randomly dispersed CFs, the investigated concentration of CFs is usually below 10 vol. %.

However, it is not only the concentration of the conductive fillers that affect the percolation, the orientation of the CFs also plays an important role. It has been found that, if the orientation of the CFs are the higher, the percolation threshold will shift to higher concentration [5]. To realize the short cut CFs with highly orientation in the composite, the melt spun method will be chosen in this work.

Hyytiä has presented a report about continuum percolation, in which a system with totally aligned cylinder was assumed. In their work, under ideal circumstances, the percolation threshold φ_c was equal to 28.19 vol. % [6]. The study was actually based on the "Swiss cheese" model (The percolation of bubbles inside the cheese to connect each other) from Lorenz [7]. The soft cylinders in the study can „assimilate" into the others to form a pathway, which is impossible to be achieved for the rigid CFs in practical situation. Still, the merit of this model is to explain why the percolation threshold for aligned cylinder fillers is located at higher concentration, which were rarely reported before.

Besides this model, the percolation threshold of composite with highly orientated CFs is still unclear. Therefore in this work, PMMA/CF composite were melt spun, to produce composite fibers with highly orientated CFs (fibers in fiber), and the electrical conductive properties under room temperature were measured.

2. Experimental methods

The matrix material is PMMA Plexiglas 7N (Evonik Röhm GmbH, Germany) with weight average M_w = 99 kg/mol, Polydispersity Index = 1.52. Chopped carbon fibers were from Tenax® - JHT C493 6mm (Toho Tenax Europe GmbH) of 7 µm diameter, with a specific resistance of 1.7×10^{-3} Ω/cm.

All the materials were firstly dried under vacuum at 80 ˚C, and with particular proportion melt mixed in kneader PolyDrive (Haake, 557-8310) for 10 min at 200 ˚C, with a rotation speed of 60 min^{-1}. After melt mixing the composites were smashed into granules, and dried under vacuum at 80 ˚C for 24h. The resulting CF concentration of composites was determined by thermogravimetric analysis (TGA).

The composite granules after drying were melt spun under 200 ˚C with the capillary rheometer (Göttfert, Rheograph 2003), with an extrusion speed of 0.08 mm/s. The die of the capillary rheometer was chosen to have a length of 10 mm and a diameter of 1 mm. The extruded composite fibers and the corresponding granules were dissolved in acetone to prepare cast films. The advantage is, that one can directly investigate the CFs using a light microscope (Leitz, Orthoplan P) and the software JMicrovision. 500 carbon fibers were randomly chosen and measured with respect to the length to reveal the distribution of CFs for each sample. The photos of the cross section after breakage were taken with a SEM (Leica, LEO 435VP). The direct current conductivity of the extruded composite fibers was measured at room temperature. The extruded composites were cut to pieces of length of 2 cm, at least 10 samples were randomly chosen and measured. Besides, some samples were coated with silver, to make comparisons with those samples without coating (Fig. 1).

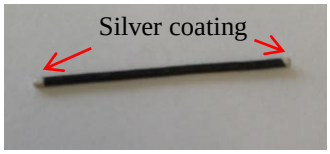

Figure 1. Samples with Silver coating on the both ends.

3. Results and discussion

3.1 Morphology of the composite

Fig. 2 shows the cut CFs on the surface of the composite fiber, which has an ordered arrangement and orientation for CFs. Besides, the CFs point out of the surface of the composite and are not covered with polymer. It can be assumed, that no further preparations (e.g. silver coating) are needed for the conductivity measurement.

The sections of a composite fiber with different concentration of CFs are shown in Fig. 3 (a)-(f). The CFs from Fig. 3 (a) and (b) have a highly orientation inside the composite fiber, and the CFs are mostly parallel to each other. The small holes from the photos are the position, where the CFs were pulled out and got lost during the sample preparation. It can been seen from Fig. 3 (a), the CFs are rarely connected, even the concentration of CFs reaches almost 10 vol. %. The conductivity of the composites depends on the amount of "pathway", which is built by connection of CFs with each other. However under this circumstance (Fig. 3 (a)), the amount of "pathway" in composites is not enough, i. e. the composites are not conductive (still above the conductivity of the pure matrix material PMMA).

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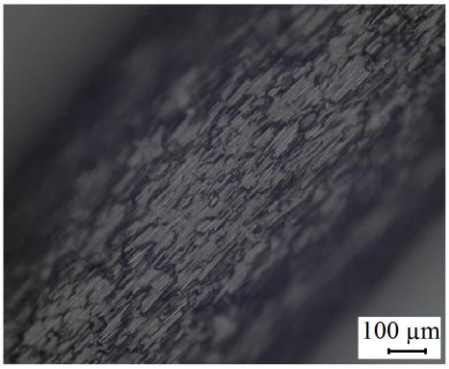
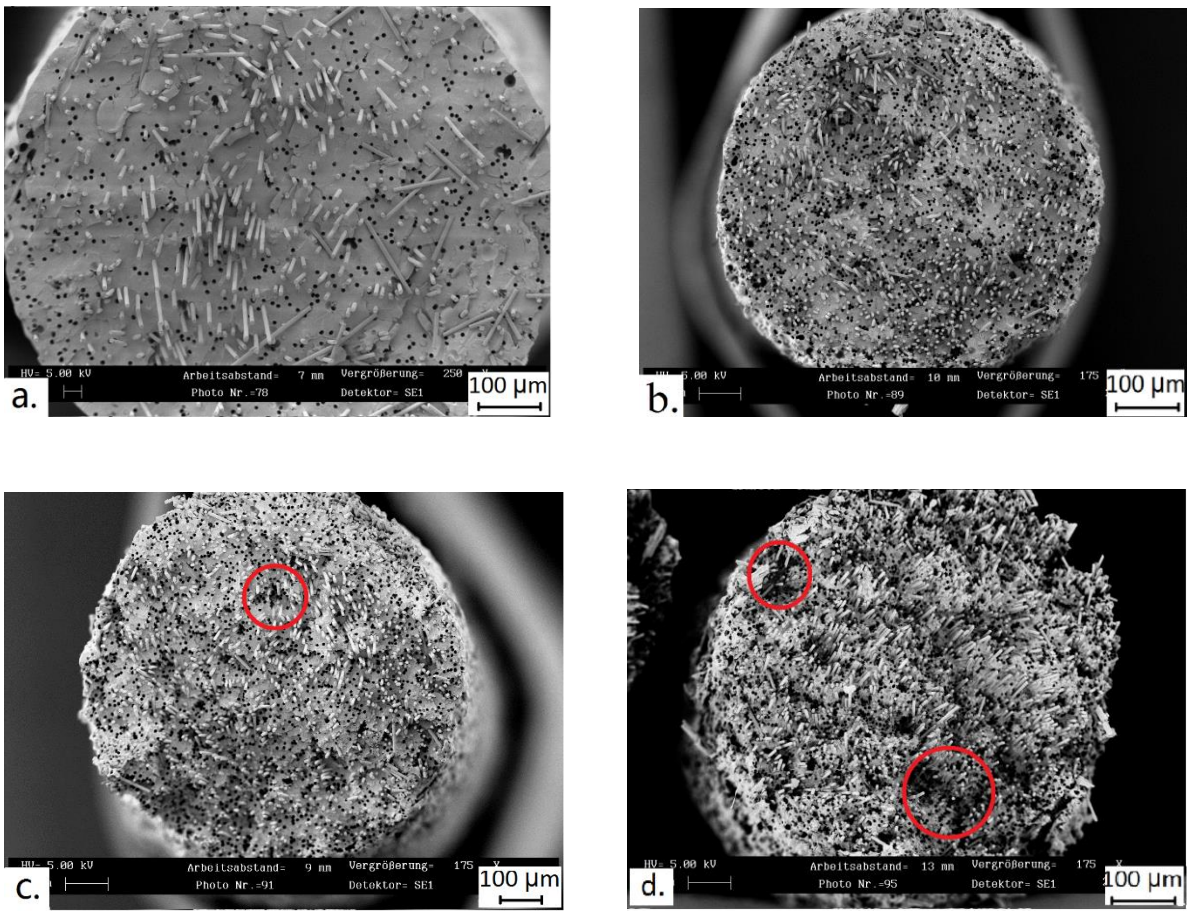


Figure 2. Surface of the composite fiber with highly orientated CFs, with 9.83 vol. % CF

It should be noted, that some CFs gathered themselves together (bunch of CFs), and were lost during the breakage of the sample, which leads to "big black holes" on the picture (marked with red circles).This is an obvious signal for the contact between the CFs. The "big black holes" firstly shows up from 28.64 vol. % CFs (Fig. 3 (c)), which indicates the conductivity of the melt spun fibers should be changed obviously.



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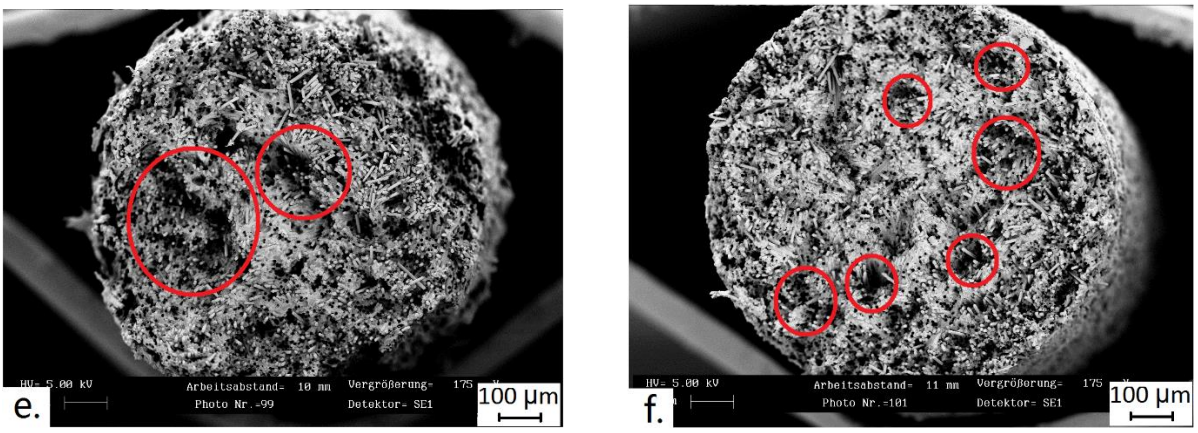

Figure 3. Cross section of composite fiber, under different concentration of CFs: (a) – 9.83 vol.%, (b) – 23.96 vol.%, (c) – 28.64vol.%, (d) – 40.2 vol.%, (e) – 46.44 vol.%, (f) – 56.44 vol.%, Red circles: gathered CFs bunch, which were lost during sample breakage.

3.2 Length of carbon fibers

In this work, CFs were produced into micrometer level through melt mixing in kneader. With the help of casting films of the composites, the length of the CFs was directly observed under a light microscope. 500 CFs were randomly chosen and the mean as well as the standard deviation was determined. The accuracy of the determined average is estimated using:

$$\Delta = 1.96 \cdot SD/N^{0.5}, \quad (1)$$

which means the true average μ is in the range [mean-Δ, mean+Δ], with a confidence of 95%. N is the number of units being studied, equal to 500 in this work, and SD denotes the standard deviation [8].

Comparisons were made between CFs from the composite granules and those from the melt spun composite fibers, in order to check if the CFs length changed during the melt spun process. Fig. 4 are samples for the statistical data. As can been seen, only slightly differences were found between these two statistical data, i. e. the melt spun process does not influence the average CFs length.

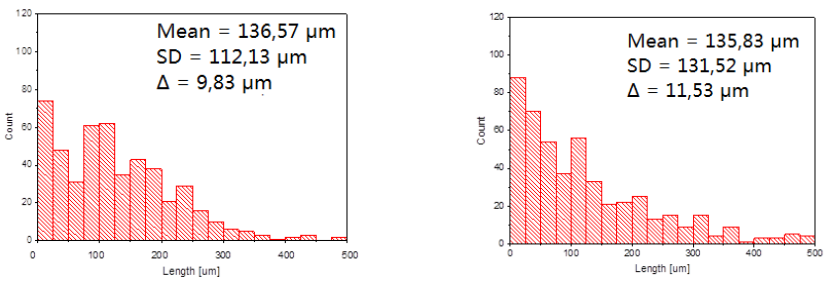

Figure 4. Statistical data of the CFs length from composite with 9.83 vol. % CF. Left: data before melt spun; Right: data after melt spun

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All the CFs length, and the real volume concentration of CFs (determined from TGA) in this work are shown in Fig. 5. When the concentration of CFs are higher, then the viscosity of the composite increase, which leads to more breakage for the CFs (i.e. shorter CFs) during melt mixing [9].

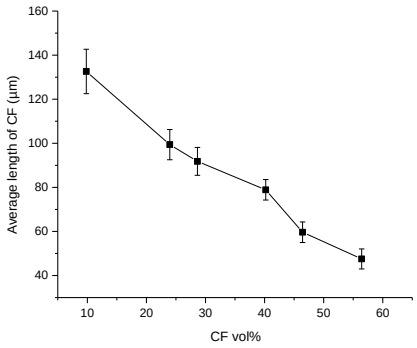

Figure 5. Relation of the average length of the CFs and the volume fraction due to stronger length degradation by higher viscosity.

3.3 Conductive property

The electrical resistance of the composites was measured at room temperature. The conductivity σ is calculated as:

$$\sigma = L/(S \cdot R), \tag{2}$$

where R is the electrical resistance of the composites. L denotes the length of the sample and S the cross sectional area. Fig. 6 shows the conductivity versus different CF volume fraction. The conductivity from the samples with silver coating differ not significant from those without coating, and is therefore not particularly noted in this work.

The maximum electrical conductivity in this work under such condition is 3.57 $S \cdot cm^{-1}$, with the 56.44 vol. % CF. The percolation threshold is then estimated between 23.96 vol. % and 28.64 vol. %. This means, the reported melt spun PMMA/CF composite fibers, are containing highly orientated CFs and therefore present a higher percolation threshold, and is consisted with the theoretical value of 28.19 vol. % [6] within the experimental error.

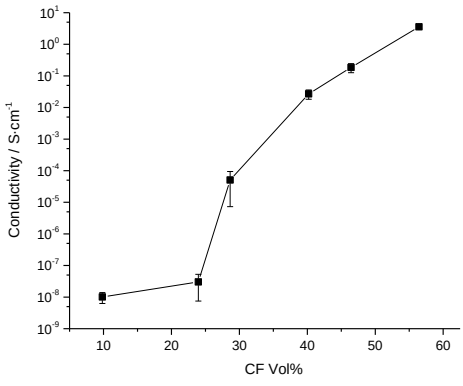

Figure 6. Conductivity vs CF volume fraction for the melt spun composites.

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4. Conclusion

In this work, PMMA/CFs were melt spun in a capillary rheometer to produce composite fibers with aligned CFs inside (fibers in fiber). The length of CFs in average from composites with different concentration of CFs was determined: The CFs length reduces, as the concentration of CFs increases; the length of CFs was not influenced during the melt spun process. Moreover, the conductivities of the composite fiber were measured, the percolation threshold was estimated between 23.96 vol. % and 28.64 vol. %.

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