Investigation of the Orientation in Composite Fibers of Polycarbonate with Multiwalled Carbon Nanotubes by Raman Microscopy

Dieter Fischer, Petra Pötschke, Harald Brünig, Andreas Janke*

Summary: The superior association of the inherent good mechanical and electrical properties makes carbon nanotubes (CNT) exceptionally interesting for the production of composite fibers of thermoplastic polymers with CNT. Alignment of the CNT in the polymer fiber is important for improved mechanical properties. Especially the production of fibers makes it necessary to get a controlled orientation and/or alignment of the CNT. We applied transmission electron microscopy (TEM) and polarized Raman microscopy to quantify multiwalled carbon nanotubes (MWNT) orientation, alignment and crystallinity in polycarbonate (PC). The evaluation of the Raman measurements provided an improved alignment orientation of the MWNT in the fibers with increasing take-up velocity during melt spinning and that the crystal structure of the MWNT is not changed through melt spinning.

Keywords: carbon nanotubes; fibers; nanocomposites; polycarbonates; Raman spectroscopy

Introduction

The global market for chemical fibers is steadily increasing with the growing world population.[1] With that the demand of new industrial fibers with special or improved properties emerges. Among other things, stronger and/or electrical conductive fibers are requested for applications as reinforcement fibers, smart clothing, electromagnetic shields or armors.[2] Addition of fillers to polymers is widely applied to make composites electrically conductive or to improve their mechanical properties. For the production of fibers with diameters between 10 and 100 μm it is necessary to use nanoscaled fillers. The superior association of their inherent good mechanical and electrical properties makes carbon nanotubes exceptionally interesting for production of polymer composite fibers. At the moment, the prices for nanotubes are still much too high for commercial use; however, the prices are dropping continuously and a breakthrough is expected within the next years. By then, it is important to develop suitable techniques for industrial polymer nanocomposite fiber fabrication. One of the most important and challenging tasks is the incorporation of the nanotubes into the polymeric matrix in order to transfer their excellent properties to the macroscopic material scale. For this purpose, single-walled carbon nanotubes (SWNT) seem to be more preferable compared to multi-walled carbon nanotubes (MWNT), because of the smaller diameter and, therefore, higher aspect ratio, the higher mechanical properties, and the possible higher load transfer because of easier bonding opportunities to polymer chains. However, the prices for MWNT are much lower than for SWNT. Thus one can assume that MWNT are closer to industrial use. For both materials, a uniform distribution and dispersion is indispensable in order to transfer the excellent properties into a polymeric matrix. For a broad technical application

Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany
E-mail: E-mail: fisch@ipfdd.de

melt mixing with subsequently melt spinning is mostly interesting. Examples are shown by Siochi et al.[3] incorporating SWNT into polyimide and Haggenmueller et al.[4] for PS/SWNT and PE/MWNT composites. Only a few examples[5,6] are shown for fibers made by incorporation of MWNT into polymer matrices following this route. However, in these examples fiber forming was performed by drawing an extrudate. With this application only low degrees of alignment could be achieved. Furthermore, no systematic investigations are known about the influencing of draw ratio achieved by melt spinning on alignment of nanotubes and mechanical properties of their composites.

From conventional fiber reinforcement it is well known that unidirectional composites show the highest improvements in strength and modulus. Therefore, it is expected that alignment of nanotubes is important for improved properties. Especially the production of fibers makes it necessary to get a controlled orientation and/or alignment of the nanotubes in macroscopic parts. Alignment is understood as a preferred orientation of a nanotube within a three-dimensional fiber. This can be accompanied by disentanglement or stretching of curved nanotubes. In order to characterize and quantify the orientation and alignment, next to TEM also polarized Raman spectroscopy and X-ray diffraction are applied, especially to fibers containing SWNT. The use of Raman spectroscopy was shown by Siochi et al.[3] and Haggenmueller.[4,7] Siochi investigated SWNT/polyimide composites and characterized the SWNT orientation characterized more or less roughly be comparison of Raman spectra parallel and perpendicular to the fiber axis and high resolution scanning electron microscopy (HRSEM) on solvent treated cross sections. The authors found an increased yield stress for the fibers with aligned SWNT respective to unoriented films. Haggenmueller et al. applied polarized Raman spectroscopy on PMMA/SWNT[7] and PE/SWNT[4] fibers and used the Raman intensity ratio of the radial breathing mode at 202 cm^{-1} parallel/perpendicular to determine the full width at half maximum (FWHM) of the distribution function. The FWHM decreased indicating enhanced alignment with reducing the fiber diameter because of higher extensional flow and lower loadings because of higher freedom to flow and to align. Sennet et al.[5] used TEM to visualize the orientation of MWNT and SWNT in PC based fibers and found regardless of the molecular weight of the PC used an increasing orientation of MWNT with draw speeds varied up to 70 m/min. The focus of our investigations was the application of polarized Raman spectroscopy accompanied by TEM for the system polycarbonate with MWNT.

Experimental

Materials and Melt Spinning

The composite of polycarbonate (PC) with 2 wt% of multiwalled carbon nanotubes (PC-2NT) was produced by diluting a masterbatch of 15 wt% multiwalled carbon nanotube in polycarbonate, supplied by Hyperion Catalysis International, Inc. (Cambridge, MA, USA), with pure PC (Lupilon E-2000, Mitsubishi Engineering Plastics) using a Haake co-rotating, intermeshing twin-screw extruder (D = 30, L/D = 10) as previously described.[8] Before processing PC was dried for at least 4 h at 120 °C under vacuum atmosphere.

Melt spinning was performed for as supplied PC Lupilon E-2000 granules and the PC based composite with 2 wt% MWNT. The melt spinning experiments were carried out by means of a self-constructed piston type spinning device. The upper part of the device consists of a drive train and a heatable cylinder with piston, closed by a single hole-die (Figure 1). The diameter of the capillary die hole was 0.3 mm, its length 0.6 mm. The adjustable speed of the piston determines the mass throughput of the molten polymer. A moveable winder is fixed below the die at a distance of 1 m to the die exit for collecting the extruded filament. The

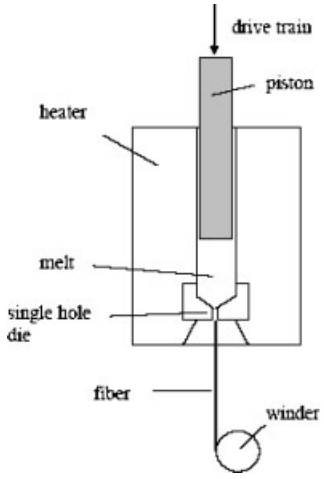

Figure 1.
Scheme of the piston-type spinning device.

winder allows changing the take-up velocity of the filament within the range of 50 until 1400 m/min.

For each run the dried material (up to 10 g) was filled under nitrogen into the cylinder and then it was heated up to the spinning temperature to get the molten state. After 10 minutes the extrusion was started. The spinning temperature for all runs was 280 °C. The take-up velocities varied between 50 m/min and 800 m/min.

Raman Spectroscopy

The spectra were collected on two different Raman microscopes. The first one was a Nikon microscope (50× objective) on the BRUKER FT Raman Module FRA 106 (connected with the BRUKER FTIR spectrometer EQUINOX 55), equipped with a Ge-detector, with an excitation laser at 1064 nm, with both the incident and the 180° backscattered light parallel to the fiber axis. The laser power was 2 mW on the sample, the laser spot 2 μm and the resolution 4 cm^{-1}. The spectra were fitted by the Levenberg-Marquardt algorithm (BRUKER OPUS software) in the range from 2000 to 200 cm^{-1}. The second one was a BH2-Olympus microscope (50× objective) on a DILOR XY Raman spectrometer, equipped with a LN_2-cooled CCD camera, with an excitation laser at 514.5 nm. The laser power was 1 mW, the laser spot 2 μm and the resolution 1 cm^{-1}. For polarized Raman spectra the fiber was rotated 90°, so that the direction of the E-vector of the polarized laser light was parallel and perpendicular oriented to the fiber axis. All spectra were baseline corrected and the peak position and intensity were fitted by the Levenberg-Marquardt algorithm (DILOR software) in the range from 1100 to 1700 cm^{-1}.

Transmission Electron Microscopy (TEM)

The fibers were imbedded into an epoxy material (Epofix). The cuts were made along the fiber axis using a Reichert Ultracut S ultramicrotom (Leica, Austria) equipped with a diamond knife with a cut angle of 35° (Diatome, Switzerland) at room temperature. An angle between fiber axis and cut axis of 35° was chosen in order to ensure no alignment induced by the cutting procedure. A relatively high thickness of 200 nm of the thin sections was chosen in order to get a good balance between a high amount of structure elements in the section and a suitable sample transparency. The TEM used is an EM 912 (Zeiss, Germany) operated at 120 kV and the micrographs were taken in defocusing contrast in order to visualize the nanotubes.

Results and Discussion

Alignment of Carbon Nanotubes along the Fiber Axis: Morphological Analysis

The spinnability of PC and the composite with 2 wt% MWNT (PC-2NT) is good; spinning and winding could be done for all experiments without problems, especially there were no filament breakages. The diameter of the fibers was quite stable as indicated by morphological analysis. Figure 2 shows TEM images of the starting PC with 2% MWNT material after extrusion and a sample after melt spinning using a take-up velocity of 400 m/min.

As can be seen from the left image of Figure 2 and as shown in a previous

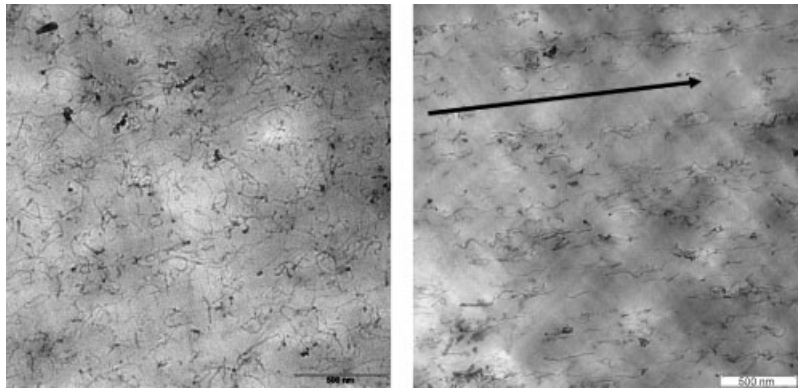

Figure 2.
TEM micrographs of a PC-2NT sample (left) and of a melt spun fiber produced with a take-up velocity of 400 m/min (right); the arrows indicate the fiber axis.

paper,[9] no MWNT orientation along the strand axis can be found in the extruded starting PC-2NT material in contrast to the right image which clearly shows orientation of the nanotubes in the length axis of the melt-spun fiber. With higher take-up velocity the length axis of the MWNT is increasingly oriented with the fiber axis even if they are not completely stretched in the axis.[10]

At higher velocities, also a tendency of fiber stretching is observable as shown in Figure 3. This MWNT orientation cannot be induced or influenced by the cutting procedures since the cut direction which is clearly seen in the images has an angle of 35° to the fiber axis.

Alignment of Carbon Nanotubes along the Fiber Axis: Raman Spectroscopy

Raman spectroscopy was applied in order to get information of the MWNT orientation, alignment and crystallinity. For interpretation the peak of the G-band at 1595 cm^{-1} which is assigned to the in-plane vibrations of the graphitic wall and the peak of the D-band at 1351 cm^{-1} originating from disorder in the graphitic structure were used. Parallel and perpendicular to the fiber axis measured Raman spectra are

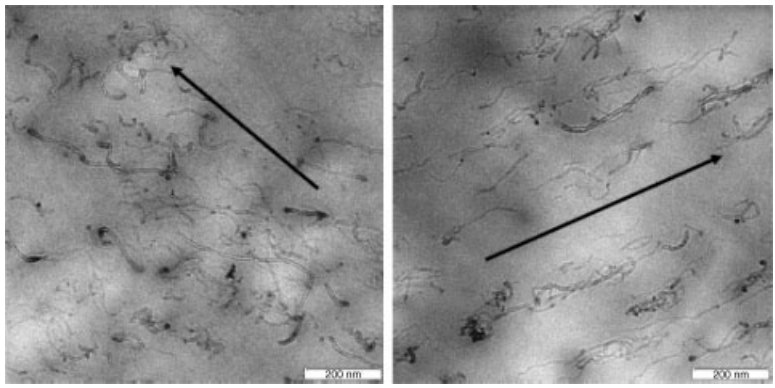

Figure 3.
TEM of thin sections indicating an alignment of the curved MWNT in the fibers with a take-up velocity of 50 m/min (left) and a take-up velocity of 400 m/min (right); arrows indicates fiber axis.

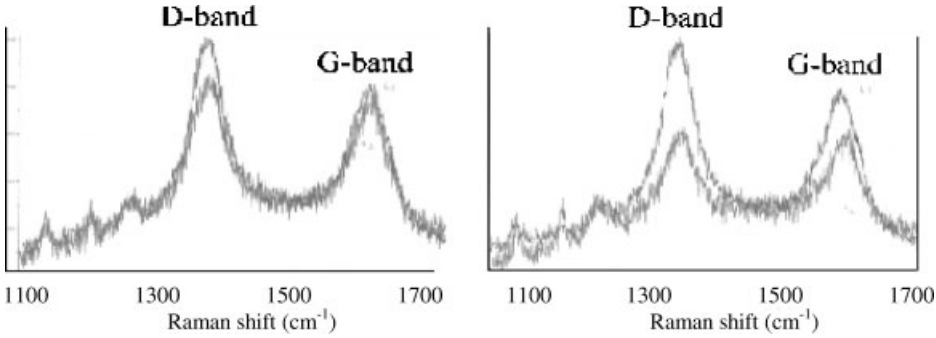

Figure 4.
Spectra of PC-2NT parallel and perpendicular to fiber axis; fiber extruded without melt spinning (left) and melt spun fiber with a take-up velocity of 400 m/min (right); upper spectra: parallel to fiber axis; lower spectra: perpendicular to fiber axis.

shown in Figure 4 for a fiber extruded without spinning and a melt spun fiber with a take-up velocity of 400 m/min.

The intensity ratio D/G is used to assess the degree of crystallinity. A lower ratio indicates a higher crystallinity. The D/G ratios were calculated and compared between the polarization direction parallel and perpendicular to the fiber axis. These D/G ratios are plotted in Figure 5 in dependence on the take-up velocity showing that all ratios for the drawn fibers are similar. That means that this ratio is more or less independent on the MWNT orientation and alignment. We can therefore conclude that the crystal structure of the MWNT is not changed through melt spinning.

The D/D and G/G ratios parallel/perpendicular to the fiber axis increases for both bands in a similar manner with the take-up velocity as shown in Figure 6.

This can be explained with an improved alignment orientation of the MWNT in the fibers through the velocity of the melt spinning. The intensity ratio can quantify the degree of orientation of the MWNT in the polymer fiber.

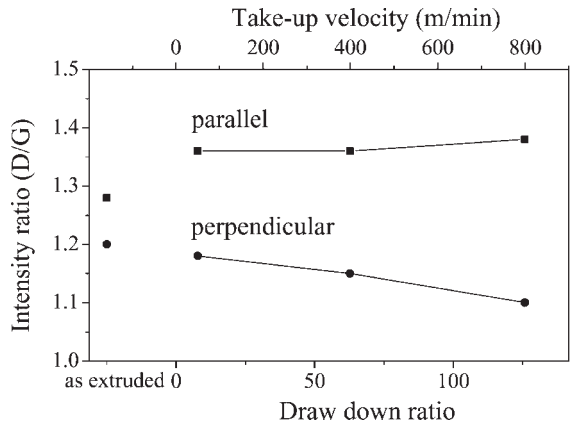

Figure 5.
Raman spectroscopy: Intensity ratios of the D and G bands in both polarization directions parallel and perpendicular to the fiber axis.

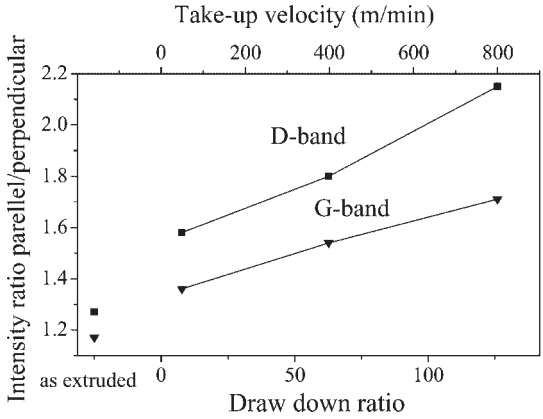

Figure 6.
Raman spectroscopy: Intensity ratios parallel/perpendicular to the fiber axis of the D band and G band.

Summary and Conclusions

Composites of polycarbonate with multi-walled carbon nanotubes and the corresponding pure PC were melt spun using a piston-type spinning device. Different take-up velocities up to 800 m/min were used. Using TEM investigations, orientation of the nanotubes length axis along the fiber axis was shown. The nanotubes align in their length axis along the fiber axis increasingly with the draw ratio; however, the curved shape of the nanotubes still exist in the melt spun fibers. However, at higher speed, the MWNT started to align by reducing their curvature. Polarized Raman spectroscopy indicated that the D/D and G/G ratios parallel/perpendicular to the fiber axis increase for both MWNT bands in a similar manner with the take-up velocity. It is possible to quantify the degree of orientation of the MWNT in the polymer fiber. Correlations of these results to electrical and mechanical properties of the PC/MWNT composite fibers are published by Pötschke et al.[10]

Acknowledgements: We thank Dr. Brzezinka (BAM Berlin) for performing the RAMAN measurements and Dr. Goering for help by their quantification.

[1] A. Marcincin, *Prog. Polym. Sci.* **2002**, *27*, 853.
[2] A. B. Dalton, S. Collins, J. Razal, E. Munoz, V. H. Ebron, B. G. Kim, J. N. Coleman, J. P. Ferraris, R. H. Baughman, *J. Mat. Chem.* **2004**, *14*, 1.
[3] E. J. Siochi, D. C. Working, C. Park, P. T. Lillehei, J. H. Rouse, C. C. Topping, A. Bhattacharyya, S. Kumar, *Comp. B* **2004**, *35*, 439.
[4] R. Haggenmueller, W. Zhou, J. E. Fischer, K. I. Winey, *J. Nanosc. Nanotechn.* **2003**, *3*, 105.
[5] M. Sennett, E. Welsh, J. B. Wright, W. Z. Li, J. G. Wen, Z. F. Ren, *Appl. Phys. A – Mat. Sci. Proces.* **2003**, *76*, 111.
[6] J. K. W. Sandler, S. Pegel, M. Cadek, F. Gojny, M. van Es, J. Lohmar, W. J. Blau, K. Schulte, A. H. Windle, M. S. P. Shaffer, *Polymer* **2004**, *45*, 2001.
[7] R. Haggenmueller, H. H. Gommans, A. G. Rinzler, J. E. Fischer, K. I. Winey, *Chem. Phys. Letters* **2000**, *330*, 219.
[8] P. Pötschke, T. D. Fornes, D. R. Paul, *Polymer* **2002**, *43*, 3247.
[9] P. Pötschke, A. R. Bhattacharyya, A. Janke, *Eur. Polym. J.* **2004**, *40*, 137.
[10] P. Pötschke, H. Brünig, A. Janke, D. Fischer, D. Jehnichen, *Polymer* in press.

