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Melt mixed SWCNT-polypropylene composites with very low electrical percolation

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Abstract

Singlewalled carbon nanotube material of the type TUBALL™ (OCSiAl) was used to prepare composites with polypropylene by melt mixing in small scale. The compression molded composites showed electrical percolation between 0.075 and 0.1 wt% and achieved volume resistivity values lower than 1 kOhm-cm already at 0.8 wt% loading. Light microscopy and scanning electron microscopy revealed good distribution and dispersion into small diameter bundles as well as retained high nanotube length. In connection with the very low percolation threshold this indicates that this SWCNT material shows an exceptional good dispersability which may be due to relatively high nanotube diameters with a mean value of 1.6 nm. In tensile tests already 0.1 wt% nanotube additions resulted in slight increases in Young's modulus and maximum stress. This SWCNT material seems to be very promising for conductivity enhancement.

Keywords:

Singlewalled carbon nanotubes, polypropylene, electrical properties, mechanical properties

Introduction

The addition of carbon nanotubes (CNTs) is a suitable was to achieve electrically conductive polymer materials whereby at the same time mechanical properties can be improved.

For industrial applications, quite often melt mixing of CNTs in thermoplastic matrices is used, representing a scalable solvent free method for which corresponding processing equipment is available in different sizes. PP is one of the mostly used low cost thermoplastic mass polymers and therefore a potential candidate for property modification by CNTs. Quite often electrical discharge or conductive behaviour is in the focus when looking for applications like e. g. housings or pipes and tubes. For this, mainly multiwalled CNTs (MWCNT) are used which differ to singlewalled CNTs (SWCNTs) in the number on concentric graphene layers and diameter of the tubes. Whereas SWCNTs have diameters of 0.5 - 2 nm and consist of only one rolled-up graphene layer, MWCNTs represent cylindrical piling-ups of SWCNTs and show typically diameters of 5 - 50 nm. Lengths are typically between 300 nm and 1-10 micrometers, leading to exceptional high aspect ratios, especially for SWCNTs. As the aspect ratio indirectly scales with the theoretical electrical percolation concentration, SWCNTs seem to be the better choice in order to achieve excellent electrical conductivity at low loadings, even if their conductivity depends on the chirality of each tube. In addition, due to the thinner diameter they are much more flexible than MWCNTs and tend in a lesser extent to length reduction during processing. Breaking of nanotubes under shear stresses in melt mixing or during ultrasonication in solution processing is increasingly considered as a phenomenon occurring during composite preparation and reducing the aspect ratio in a way, that electrical percolation threshold is increased and conductivity is decreased [1-6].

In contrast to these high expectations on the performance of SWCNT, the literature concerning electrical properties of melt mixed SWCNT- polymer composites is rare. This is connected with the fact, that the dispersion of SWCNT materials is much more difficult than that of MWCNTs. As the magnitude of the Van der Waals forces between neighbored tubes (on a per tube mass basis) increases with decreasing tube diameter the growth of SWCNTs in the formation of bundles or ropes is promoted and the resistance to dispersion in the sense of individualization into single tubes is much higher for smaller diameter SWCNTs as compared to MWCNTs. As SWCNTs also mostly have smaller diameter distributions the effect of bundling of

tubes may occur in hexagonal arrangements which are even more difficult to disperse. Thus, it seems that dispersion of SWCNTs requires quite high shear stresses which even are discussed not to be applicable during melt mixing [4]. Therefore, solution based mixing methods with the aid of ultrasound and surfactants and suitable solvents are much more preferred and reported to get reasonable dispersion of SWCNTs and individualization of the ropes.

As a consequence of this dispersion issue, in the rare studies published on melt-mixed SWCNT polymer composites, in most cases relatively bad nanotube dispersion [7, 8] and high electrical percolation thresholds are reported. Quite often morphology characterization especially in the microscale as obtained using optical microscopy is not even shown or focusing on small areas in SEM or TEM is used to judge about relatively good dispersion. For example, in polyamide 6 composites the addition of 3 wt% HiPCo-SWCNTs was needed to get percolated samples [9]. In another study on polycarbonate, HiPCo SWCNT buckypearls resulted in electrical percolation at 0.6 wt% and after pretreatment of the SWCNT buckypearls in acetone under sonication for 3 min this could be reduced towards 0.4 wt% [10, 11]. However, when using a home synthesized unpurified arc-discharge SWCNT material electrical percolation was achieved between 2 and 3 wt% loading, indicating that unbundling was not possible by the melt mixing procedure applied [10, 11]. A percolation threshold near 1 wt% was described for PP with SWCNTs from Iljin Nanotech Co. [12].

In case of melt mixing studies on PP, more frequently the effect of the SWCNT addition on the crystallization behaviour of the matrix is studied [7, 8, 13-21]. Thereby it was reported that in PP the addition of SWCNTs in most cases shows a nucleation effect and leads to an increase in the crystallisation temperatures [15, 16, 19, 21]. However, the overall crystallinity was differently influenced with SWCNT addition. Whereas Bhattacharyya et al. [7] describe an increase in crystallinity with SWCNT addition, the study of Jam and Ahangari [13] found an increase at low loadings (up to 0.5 wt%) followed by a decrease. In other studies unchanged crystallinity was found [21]. Valentini et al. [16] described an decrease of crystallinity with the SWCNT addition. The melting temperature of PP- SWCNT composites was reported either to decrease [16], increase [13] or not to change [15, 21] which may depend on PP type and its starting crystallinity and CNT source. In different studies [14, 17] the

isothermal and nonisothermal crystallization kinetics of isotactic PP was investigated. It was described that the addition of SWCNTs can reduce the crystallization half-time and increases the crystallization rate of iPP.

Studies concerning the electrical properties of PP-SWCNT composites can be found more frequently on solution mixed samples. In an intensive study Jeon et al [18] used i-PP and ethylene-propylene copolymers to evaluate the influence of PP crystallinity on SWCNT dispersion and electrical conductivity of composites, whereby the solution mixed samples were compression molded. Thereby, the content of HiPCo-SWCNTs was varied between 0.15 and 1 wt%. At the lowest content of SWCNTs investigated in this study, volume resistivity values in the range 1E9 till 1E7 Ohm-cm were achieved, whereby the material with the highest crystallinity (PP, 70%) resulted in the lowest resistivity values. The electrical percolation threshold varied from 0.25 wt% for PP with 10% crystallinity towards a value of 0.07 wt% for PP with 45 and 70% crystallinity, obtained by fitting the conductivity data with the percolation scaling law. At 1 wt% loading, the sample using PP with 70% crystallinity showed a resistivity value of ca. 1E3 Ohm-cm. Narimani et al. [12] reported for melt-mixed PP/SWCNT composites a significantly higher electrical percolation threshold of about 1 wt.% SWCNT.

The morphology of PP/SWCNT composites melt-mixed in small-scale was regarded in a study by Leelapornpisit et al. [8] which was focussed on the influence of SWCNTs (0.25 -1.0 wt%) on crystallization and dynamic-mechanical behaviour. Scanning electron microscopy on cryo fractured surfaces together with optical microscopy showed well-dispersed nanotube ropes next to small and large agglomerates (up to 50 micrometers at 0.25 wt% loading). Bhattacharyya et al. [7] showed in composites with 0.8 wt% HiPCo SWCNTs using light microscopy also a significant amount of nanotube agglomerates. A worse SWCNT macrodispersion was also shown by Ghorbanzadeh et al. [14] and Radhakrishnan et al. [17]. Valentini et al. [21] found a large amount of thick SWCNT bundles in melt mixed PP/SWCNT composites observed using SEM.

By introducing a new type of SWCNT material with the trade name TUBALL™ from the company OCSiAl LTD. a new high quality SWCNT product came into market, which dispersion and electrical percolation behaviour in polypropylene is shown in this study using melt mixing in small scale.

Experimental part

Material

Pristine SWCNTs TUBALL™ material synthetized using CVD process is provided by OCSiAl (www.ocsial.com). A polypropylene (PP) homopolymer Moplen HP400R (basell) was used having a melt flow rate of 25 g/10 min at 230°C and 2.16 kg. The as received PP granules were either used as received or milled using a Retzsch mill and only powder particles with sizes smaller than 1 mm achieved by sieving was used.

Methods

Structural and morphological features of SWCNTs were studied using High-Resolution Transmission Electron Microscopy (HRTEM). Samples for HRTEM were prepared by dropping SWCNT powder suspension in water on a copper carbon grid. HRTEM observation were performed using a JEM-2010 device (JEOL Co.), equipped with a field emission gun, operating at 200 kV and with a point resolution of 0.14 nm.

The purity of the SWCNTs was determined by Thermogravimetric Analysis (TGA). Solid samples of approximately 5 mg were measured using a Netzsch STA 449 F1 Jupiter at a heating rate of $5°C \cdot min^{-1}$ in the temperature range of 25-950°C under air atmosphere.

The purity, quality and diameter size distribution of the SWCNTs were obtained using Raman spectroscopy. Raman spectra were measured using a Horiba JY LabRam HR800 confocal Raman microscope with 633, 514 nm, Horiba T6400 with 488 nm and Bruker FT-Raman module RAMII integrated with FTIR spectrometer Vertex 80 with 1064 nm laser excitation wavelength.

The electrical resistivity of pure CNT powder was measured using PuLeMe (Pulverleitfähigkeitsmessung) instrument, developed and constructed at the Leibniz Institute of Polymer Research Dresden. The powder was filled into a cylinder (40 mm length, 5 mm diameter) and compressed by a piston up to a pressure of 30 MPa using a stepper motor. During the compression process, the electric resistance is continuously measured between two gold electrodes located on top of the piston and on the bottom of the cylinder using a Keithley 2001 electrometer. The resistivity measurements are carried out as 4-point-technique (resistance lower than 1000

Ohm) or as 2-point-technique (resistance higher than 1000 Ohm) whereas the switching is done programmatically based on the detected measurement data. The control of the device as well as the data acquisition and analysis is carried out by custom-made software based on Agilent VEE Version 9.3. [22].

Morphological characterization the composites was performed using scanning electron microscopy (SEM) using anUltra plus microscope, Carl Zeiss GmbH, Germany with a field emission cathode. The composite samples were cryofractured and platin sputtered. SEM data for morphological characterization of pristine TUBALL™ powder was carried out using LEO 1430 VP Carl Zeiss GmbH electron microscope with 3 nm resolution.

Melt compounding of dry premixed PP granules or powder and carbon nanotube powdery material was performed using a conical twin screw micro-compounder Xplore DSM15 (capacity of 15 ccm) at a mixing temperature of 210°C, rotation speed of 250 rpm and mixing time of 5 min. After mixing the material was led out as a strand without additional cooling. Next to direct incorporation, also the strategy of masterbatch diluting was investigated. Therefore, a masterbatch containing 2 wt% of SWCNT was produced in the first step, which afterwards was diluted towards 0.1 wt%. Both steps were performed under the conditions named above using PP powdery material.

Electrical measurements were performed on pressed plates with a thickness of 0.5 mm and a diameter of 60 mm (pressing conditions: 210°C, 2 min, press PW40EH (Otto-Paul-Weber GmbH, Germany). For composites with resistivity >1E7 Ohm-cm a Keithley text fixture 8009 and for conductive samples a 4-point text fixture with gold electrodes with a distance of 16 mm between the source electrodes and 10 mm between the measuring electrodes were used combined with a Keithley electrometer E6517A.

The state of CNT macrodispersion in the composites was studied using light transmission. Thin sections of 5 µm thickness were prepared in perpendicular direction to the extruded strand using a Leica RM 2265 microtome (Leica Microsystems GmbH, Germany) and were fixed with Aquatex® on glass slides. The samples were characterized with a microscope BH2 in transmission mode combined with a camera DP71 (Olympus Deutschland GmbH, Germany).

Dynamic scanning calorimetry (DSC) was performed on compression molded samples using a DSC Q 1000 von TA Instruments using Heating-Cooling-Heating cycles at 10K/min in N2 atmosphere using a DSC Q100 instrument (TA Instruments). Crystallinity was calculated from the heat capacity in the second heating run, corrected for polymer content. The crystallinity was calculated with the value of 207 J/g for 100% crystalline PP [23]. The onset temperature of crystallization, $T_{c,0}$ and the maximum crystallization temperature, $T_{c,m}$ were also determined.

Mechanical properties were measured according to DIN EN ISO 527-2/S3a/10 using Zwick UPM Universal Testing Machines at Force of 1 kN and testing velocity of 10 mm/min on 6-8 miniature tensile bars cut from the pressed plates.

Results

SWCNT characterisation

TUBALL™, representing an as-produced single-walled carbon nanotube material manufactured by OCSiAl was used as the conductive filler in this study. Scanning electron microscopy (SEM) of pristine SWCNTs powder and High-resolution transmission electron microscopy (HRTEM) of pristine SWCNTs is demonstrated in Fig. 1 A and B, respectively. SEM illustrates a primary character of TUBALL™ powder, which consists from extended structures with a high purity. While, the HRTEM ~~image~~ shows ~~that the material consists~~ that these extended structures are the ~~of~~ bundles of single-walled nanotubes (inset of Fig. 1) with an average diameter from 20 to 50 nm.

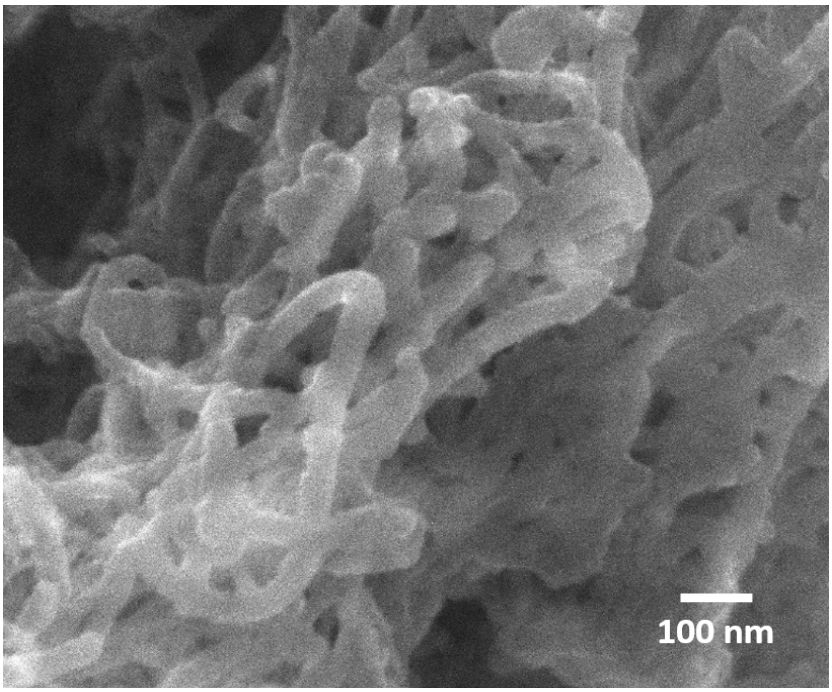

Fig.1-A. SEM image of pristine SWCNTs produced by OCSiAl.

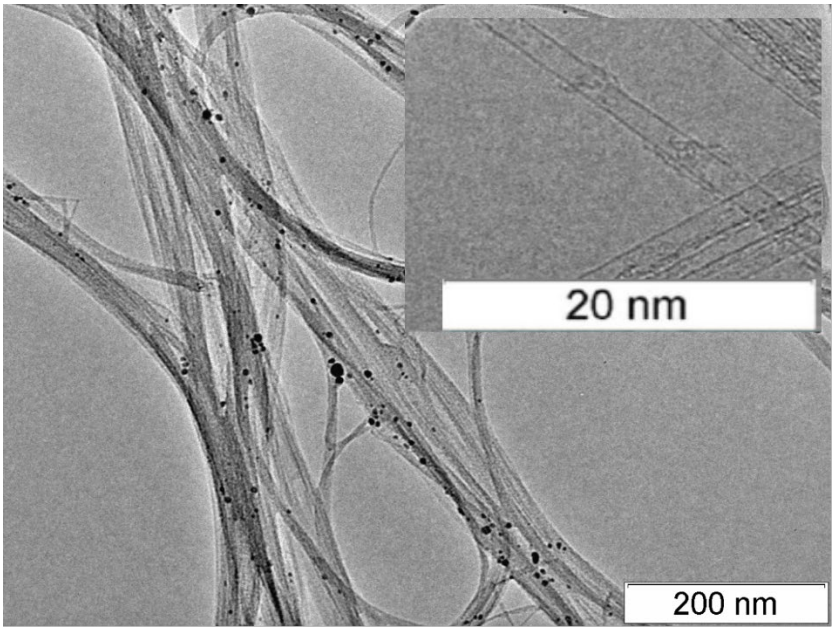

Fig. 1-B. HRTEM images of SWCNTs produced by OCSiAl.

The purity of SWCNTs has been investigated using TGA (Fig. 2). TGA curve (black) has only one weight loss around at 78 wt.% showing that the catalytic iron particles content is around 15 wt.%. These inorganic (Fe) impurities are virtually encapsulated by carbon. It is known that these particles can be oxidized to iron oxide at temperatures higher than 200°C. This leads to a slight increase in the sample mass observed in the range between 250 and 400°C. This increase in the TGA curve has a weak character as the burning process of amorphous carbon (< 1wt%) starts at the

same conditions. Finally, the TGA curve shows that the oxidation of SWCNTs is starting at around 450°C with a maximum oxidation rate at 640°C according to the derivative function (blue).

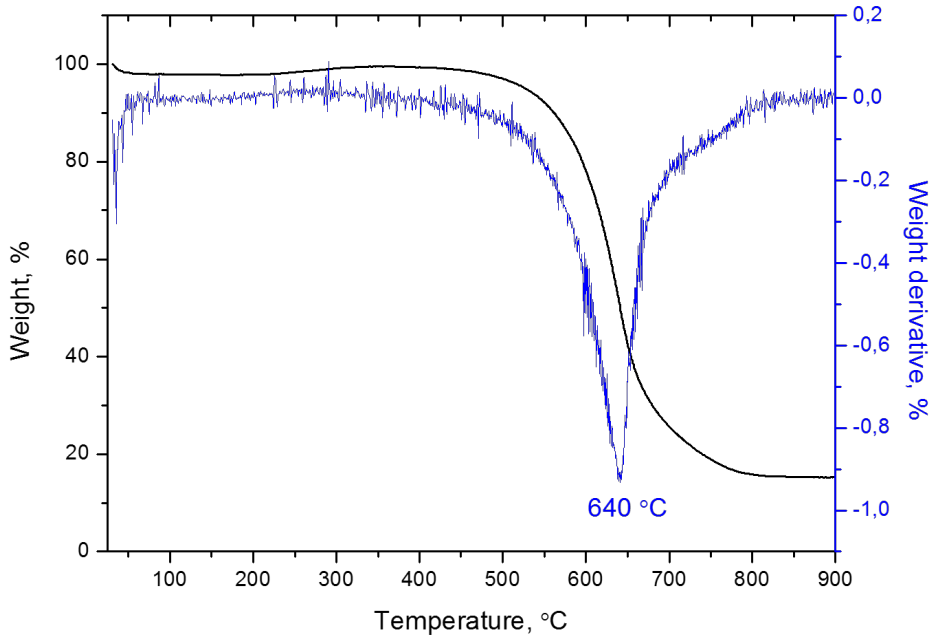

Fig. 2. TGA curves of pristine SWCNTs

Raman spectroscopy has been applied for obtaining further information concerning the purity, quality and diameter size of pristine SWCNTs (Fig. 3) [24]. The two peaks situated at 1590 cm^{-1} and 1348 cm^{-1} are attributed to the G and D bands respectively. The G-band is attributed to the vibrations of sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice of a graphitic layer. While the D-band is sensitive to structural defects in the graphitic sp^2 layer, which is typical for defectiveness of CNTs and carbonaceous impurities such as amorphous carbon particles. Taking this into account, the value of the intensity ratio between the G and D bands significantly shows the presence of defects and impurities in the SWCNTs. The observed G/D intensity ratio value of 100 shows the high purity and quality of the SWCNTs used in this study. The Radial Breathing (RBM) Modes distribution measured at 1064, 633, 514 and 458 nm laser wavelength (data is not shown here) shows that SWCNTs diameter varies in the range of 1 - 2.2 nm with a maximum at 1.6 nm SWCNT diameter size.

The length of the nanotubes was measured using AFM to be larger than 5 micrometer [25].

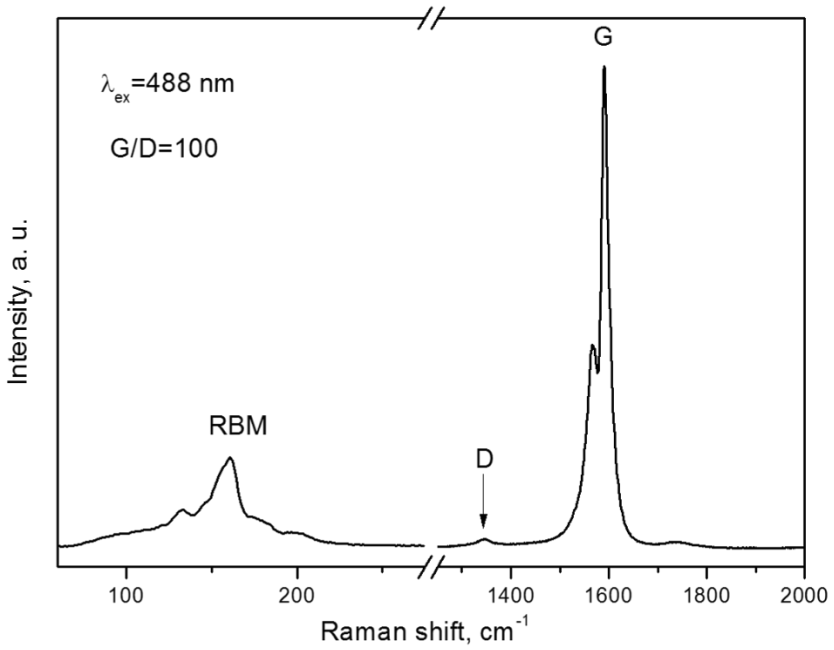

Fig. 3. Raman spectrum of pristine SWCNTs

Additionally, the electrical conductivity of the SWCNT powder was measured to be 13.9 S/cm at 30 MPa. This value is in the range which was also measured for multiwalled CNT powders (4-30 S/cm) [22, 26].

Characterisation of PP composites

The electrical volume resistivity of directly mixed PP(powder)/SWCNT composites as shown in Fig. 4 illustrates an unexpected low electrical percolation threshold. Starting from an initial resistivity of 1E17 Ohm-cm for pure PP, a very distinct decrease of resistivity occurs already between 0.075 wt% and 0.1 wt% SWCNT addition, which indicates the range of electrical percolation. The resistivity value achieved at the loading of 0.1 wt% is already lower than 1E5 Ohm-cm and at 0.8 wt% addition, values lower than 1 kOhm-cm are reached. This percolation threshold is much lower than that one of 1 wt% reported by Narimani and Hemmati [12] for PP melt mixed composites with SWCNTs produced by Iljin Nanotech Co. A comparable finding of such very low percolation was only described in a study by Andrews et al. [27] on PP/MWCNT composites produced by shear mixing, where a decrease of electrical surface resistivity was found already at an addition of 0.05 vol% (~0.1 wt%)

MWCNTs. Other authors found significantly higher electrical percolation thresholds for PP/multiwalled CNT composites [28-32].

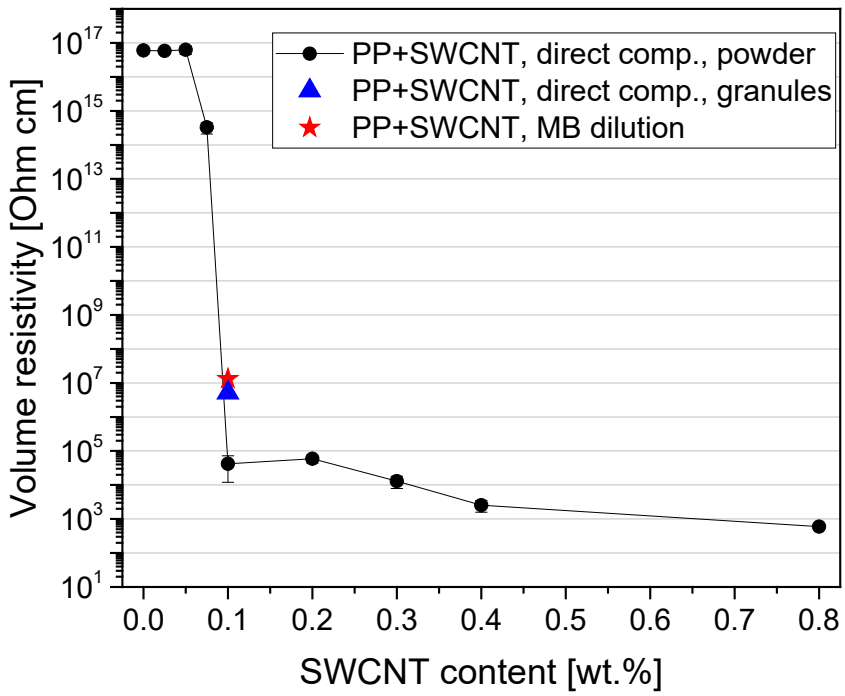

Fig. 4: Electrical volume resistivity vs. SWCNT content in PP based composites prepared using different melt-mixing strategies

The macrodispersion of 0.1 wt% SWCNT in PP composite was studied using transmission light microscopy (Fig. 5). Despite the low SWCNT content some small non-dispersed agglomerates were visible, illustrating non-perfect dispersion. However, compared to the rare literature observations (e.g. [7]) this state of macrodispersion appears to be very good. In combination with the extremely low electrical percolation threshold it can be concluded that this SWCNT material also shows a suitable SWCNT dispersion in the nanoscale, thus enabling electrical percolation at this low loading.

The observation of cryo-fractured surfaces using scanning electron microscopy, as shown exemplarily in Fig. 6 for 0.4 wt% SWCNT, illustrates well distributed nanotubes with different diameters. As the tube diameters appear larger than expected from single tubes, it seems that most of them are still organized in relatively thin bundles. Interestingly, the length of the visible nanotubes is in many cases larger than 2 µm, indicating longer real nanotube length as nanotube parts may be buried in

the matrix. The resulting high nanotube aspect ratio is favourable for electrical percolation at low loadings and may be next to the good state of macrodispersion a reason for the very low electrical percolation threshold.

The results obtained for the direct SWCNT incorporation at 0.1 wt% loading were compared with composites which were prepared using the masterbatch approach. In that case the nanotubes experience twice the shearing within the compounder. The nanotube dispersion is thereby generally expected to be better. This is also found as indicated by the lower number of (very small) remaining agglomerates in light microscopy investigations (Fig. 5). The very low electrical resistivity of samples with 0.1 wt% SWCNT could be confirmed, even if the value of resistivity is with 1E7 Ohm-cm slightly higher than that of the sample produced by direct incorporation. This may be due to the higher mixing energy input which, despite better resistance of SWCNTs against breakage, may lead to more pronounced nanotube shortening. Such breakage behaviour was shown for MWCNTs [5, 6, 33] after melt mixing. In addition, it was investigated if the results are different when the PP was applied in the granule shape as compared to the powder shape. With PP granules premixed with the SWCNT powder, again at 0.1 wt% loading electrical percolation and electrical resistivity values of 5E6 Ohm-cm were achieved. These values are slightly higher than those when applying powdery PP indicating that the starting PP material size has a small influence. The CNT macrodispersion is as good as when using PP as powder (Fig. 5).

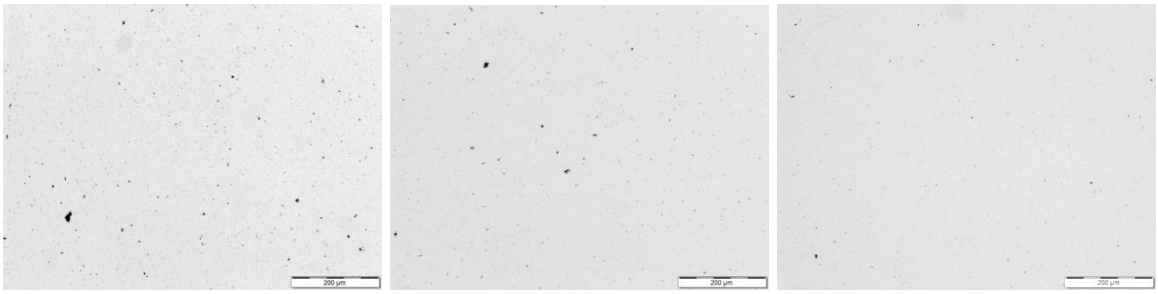

Fig. 5: Light transmission observation of thin sections of PP-0.1 wt% SWCNT composites prepared using PP powder (left), PP granules (middle) and using masterbatch dilution with PP powder (right)

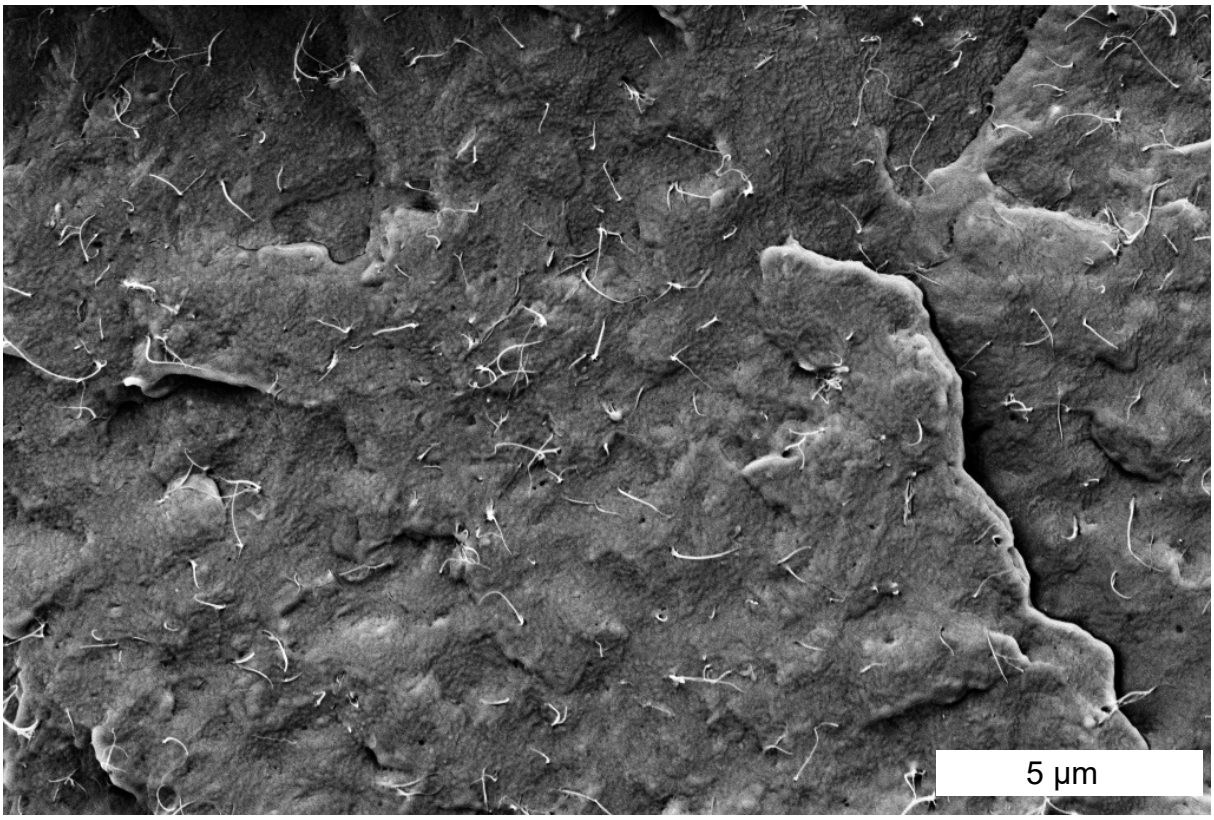

Fig. 6: Scanning electron microscopy image of a cryofractured of PP-0.4 wt% SWCNT composite (PP powder)

Furthermore, tensile tests were performed to study the influence of 0.1 wt% loading also on the stress-strain behaviour. The comparison of mean curves of the unfilled PP and PP/0.1 wt% SWCNT composite is shown in Fig. 7. It was found that the incorporation of 0.1 wt% SWCNT leads to slight increase of the elastic modulus E_t from 1632±82 MPa up to 1918±80 MPa. The maximal stress σ_{max} increased slightly from 32.8±1.3 MPa up to 34.6±0.9 MPa, whereby elongation at break was unchanged. Relatively high scattering of the values is due to the fact, that miniature dog-bones were used.

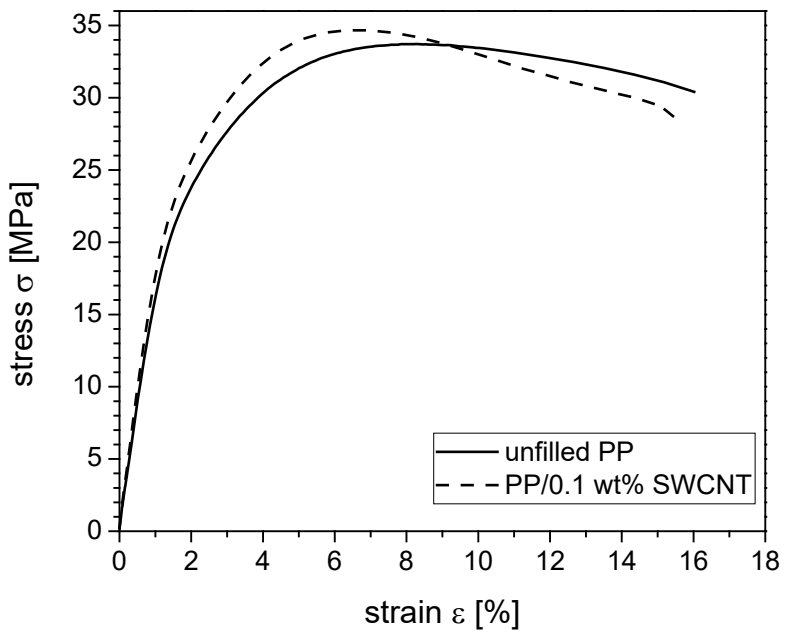

Fig. 7: Stress-strain behavior of PP and PP-0.1wt% SWCNT (PP powder)

DSC measurements indicated that the addition of SWCNT has effects on the crystallinity of PP composites, the melting temperature and the crystallisation temperature. As shown in Table 1, all values increase as compared to powdery PP processed under the same conditions. Already the incorporation of 0.1 wt% SWCNT leads to an increase of 10 K for the onset as well as maximum crystallisation temperature. For the PP containing 2 wt% SWCNT the crystallisation temperatures increase by 16-17 K. Interestingly, also the melting temperature increased with the SWCNT addition by 3-4 K. The same tendencies were also described from different authors [8, 13, 17, 21], whereas the increases of the crystallisation temperature found in these studies were not so pronounced like in our study. This again supports better states of dispersion and more nanotube surface available for nucleation.
Furthermore, as seen in Table 1 the crystallinity of PP increased with the addition of 0.1 wt% SWCNT by about 3% (absolute) and stayed nearly constant at higher loadings. Compared to literature on melt-mixed PP-SWCNT composites, Valentini et al. [21] described for unchanged values of PP crystallinity by 5-20 wt% SWCNT addition. In contrast, Jam et al. [13] found an increase of the PP crystallinity with SWCNT addition of 0.5 wt% (36.8 to 40.2%) followed by a decrease with further increasing SWCNT content up to 5 wt% (towards 37.9%). Such differences may be due to the different PP and SWCNT types used, in which the surface of the

nanotubes, also dependent on the state of dispersion, influences the nucleation ability differently. It is obvious that the effect found in our study is exceptional high as compared to other studies on melt mixed composites. The DSC results indicate that also the slightly enhanced crystallinity may contribute to the somewhat improved mechanical properties.

Table 1: DSC results for PP and PP-SWCNT composites prepared by direct incorporation from PP pwders

	T_m [°C]	$T_{c,\ onset}$ [°C]	$T_{c,max}$ [°C]	ΔH_c [J/g polymer]	crystallinity [%]
Processed PP	160.8	123.7	120.8	100.3	48.5
PP + 0.1 wt% SWCNT	164.2	134.3	131.2	106.9	51.6
PP + 0.2 wt% SWCNT	164.1	133.3	130.0	106.1	51.3
PP + 0.3 wt% SWCNT	164.9	135.3	131.9	105.8	51.1
PP + 0.4 wt% SWCNT	165.2	137.3	133.7	104.4	50.4
PP + 2 wt% SWCNT	167.0	140.8	136.8	105.6	51.0

Summary

In this study, the properties of pristine single-walled carbon nanotube material and their melt mixed PP composites were investigated. The SWCNTs were characterized by HRTEM, TGA and Raman spectroscopy. The characterization of CNT macrodispersion by light microscopy indicated only some small residual nanotube agglomerates in the composite. Nevertheless, excellent material properties could be found. A very low electrical percolation threshold of 0.075-0.1 wt% was detected which was not reported before for PP/SWCNT composites. This low threshold could be confirmed when using PP granules instead of powder and when applying the masterbatch approach.

As reason for this an exceptional good dispersability is assumed, as nearly no agglomerates could be observed in light microscopy observations and SEM investigations indicated good distribution and dispersion into small-sized bundles. This may be related to the relatively high SWCNT diameters of ca. 1.6 nm. In addition, the high nanotube length seems to be retained after melt mixing. The nucleation efficiency is larger than reported in other studies of PP with SWCNTs, supporting the aspect of very good dispersability and higher nucleating surface area of this kind of SWCNT.

The addition of SWCNT leads to a slight improvement of the mechanical properties. This increase may be contributed by the slightly increased crystallinity found already at 0.1 wt% loading.

The results indicate that TUBALL SWCNT material is very effective filler for polypropylene, and it may be applied also in other thermoplastic polymer matrices. It disperses well and show electrical conductivity at extremely low loadings. Further and more detailed investigations are planned.

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References

1. Pötschke P, Villmow T, and Krause B. Polymer 2013;54(12):3071-3078.
2. Guo J, Liu Y, Prada-Silvy R, Tan Y, Azad S, Krause B, Pötschke P, and Grady BP. Journal of Polymer Science Part B: Polymer Physics 2014;52(1):73-83.
3. Vasileiou AA, Kontopoulou M, Gui H, and Docoslis A. Acs Applied Materials & Interfaces 2015;7(3):1624-1631.
4. Huang YY and Terentjev EM. Polymers 2012;4(1):275-295.
5. Socher R, Krause B, Müller MT, Boldt R, and Pötschke P. Polymer 2012;53(2):495-504.
6. Krause B, Villmow T, Boldt R, Mende M, Petzold G, and Pötschke P. Composites Science and Technology 2011;71(8):1145-1153.
7. Bhattacharyya AR, Sreekumar TV, Liu T, Kumar S, Ericson LM, Hauge RH, and Smalley RE. Polymer 2003;44(8):2373-2377.
8. Leelapornpisit W, Ton-That M-T, Perrin-Sarazin F, Cole KC, Denault J, and Simard B. Journal of Polymer Science Part B: Polymer Physics 2005;43(18):2445-2453.
9. Bhattacharyya AR, Pötschke P, Haussler L, and Fischer D. Macromolecular Chemistry and Physics 2005;206(20):2084-2095.
10. Pötschke P, Bhattacharyya AR, Janke A, Pegel S, Leonhardt A, Taschner C, Ritschel M, Roth S, Hornbostel B, and Cech J. Fullerenes Nanotubes and Carbon Nanostructures 2005;13:211-224.
11. Pötschke P, Hornbostel B, Roth S, Vohrer U, Dudkin SM, and Alig I. AIP Conference Proceedings 2005;786:596-601.
12. Narimani A and Hemmati M. Polymers & Polymer Composites 2014;22(6):533-540.
13. Jam JE and Ahangari M. Polymer-Plastics Technology and Engineering 2012;51(12):1186-1192.
14. Ghorbanzadeh Ahangari M, Fereidoon A, Kordani N, and Garmabi H. Polymer Bulletin 2011;66(2):239-258.

15. Manchado MAL, Valentini L, Biagiotti J, and Kenny JM. Carbon 2005;43(7):1499-1505.
16. Valentini L, Biagiotti J, Kenny JM, and Santucci S. Journal of Applied Polymer Science 2003;87(4):708-713.
17. Radhakrishnan VK, Davis EW, and Davis VA. Polymer Engineering & Science 2010;50(9):1831-1842.
18. Jeon K, Warnock S, Ruiz-Orta C, Kismarahardja A, Brooks J, and Alamo RG. Journal of Polymer Science Part B: Polymer Physics 2010;48(19):2084-2096.
19. Razavi-Nouri M. Journal of Applied Polymer Science 2012;124(3):2541-2549.
20. Kang DW and Ryu SH. Polymer International 2013;62(2):152-157.
21. Valentini L, Biagiotti J, Kenny JM, and Santucci S. Composites Science and Technology 2003;63(8):1149-1153.
22. Krause B, Boldt R, Häußler L, and Pötschke P. Composites Science and Technology 2015;114:119-125.
23. Gaur U and Wunderlich B. Journal of Physical and Chemical Reference Data 1981;10(4):1051-1064.
24. Lopez-Lorente AI, Simonet BM, and Valcarcel M. Analyst 2014;139(1):290-298.
25. Technical Datasheet Tuball TM, OCSiAl LTD., accessed February 11th, 2016, http://ocsial.com/assets/documents/TDS_TUBALL_4iN0GUh.pdf
26. Arjmand M, Chizari K, Krause B, Pötschke P, and Sundararaj U. Carbon 2016;98:358-372.
27. Andrews R, Jacques D, Minot M, and Rantell T. Macromolecular Materials and Engineering 2002;287(6):395-403.
28. Seo M-K and Park S-J. Chemical Physics Letters 2004;395(1-3):44-48.
29. Wang Z, Fan X, Wang K, Deng H, Chen F, and Fu Q. Composites Science and Technology 2011;71(11):1397-1403.
30. Garzón C and Palza H. Composites Science and Technology 2014;99:117-123.
31. Besco S, Lorenzetti A, Hrelja D, Boaretti C, Roso M, Ferri D, and Modesti M. Macromolecular Materials and Engineering 2014;299(7):814-824.
32. Zhong J, Isayev AI, and Huang K. Polymer 2014;55(7):1745-1755.
33. Krause B, Boldt R, and Pötschke P. Carbon 2011;49(4):1243-1247.