

Thermoplastic polyurethane • Carbon nanotubes • Nanocomposite • Melt mixing

Recently, carbon nanotubes (CNT) have been shown to be attractive fillers for achieving electrical conductivity of polymers at relatively low CNT contents. Amounts lower than 1 wt% are reported to be sufficient to get conductive polymers which is much less as compared to carbon black. This efficient behavior of CNT is caused by the excellent electrical properties in combination with the very high aspect ratio, as high as 1000. In addition, mechanical properties may be enhanced due to the fiber like shape of the filler. Thus, it is also promising to use CNT as additives in polyurethanes for electrically conductive or antistatic applications. The aim of this study is the melt modification of a commercial thermoplastic polyurethane using different multi-walled carbon nanotubes and the study of electrical, mechanical, and thermal properties of the nanocomposites.

Thermoplastisches Polyurethan mit Kohlenstoff-Nanoröhren für elektrisch-dissipative und leitfähige Anwendungen

Thermoplastisches Polyurethan • Kohlenstoff-Nanoröhrchen • Nanokomposit • Schmelzemischen

In letzter Zeit konnte gezeigt werden, dass Kohlenstoff-Nanoröhren (Carbon Nanotubes, CNT) ein attraktiver Füllstoff zur Leitfähigkeitsausrüstung von Kunststoffen bei niedrigen Zugabemengen sind. Es wurde berichtet, dass Gehalte kleiner als 1 Gew% zum Erreichen von Leitfähigkeit ausreichend sind, was deutlich weniger ist als bei Leitrußen. Dieses effektive Verhalten von CNT liegt in ihren exzellenten elektrischen Eigenschaften und dem sehr hohen Aspekt-Verhältnis bis zu 1000 begründet. Zusätzlich können mechanische Eigenschaften der Verbunde durch die faserförmige Form des Füllstoffes verbessert werden. Daher ist es auch vielversprechend, CNT als Additive in Polyurethanen einzusetzen um elektrisch leitfähige oder antistatisch ausgerüstete Materialien zu erhalten. Das Ziel dieser Untersuchungen ist die Schmelzmodifizierung eines kommerziellen thermoplastischen Polyurethans mit verschiedenen mehrwandigen CNT und die Untersuchung von elektrischen, mechanischen und thermischen Eigenschaften der Nanokomposite.

Thermoplastic Polyurethane Filled with Carbon Nanotubes for Electrical Dissipative and Conductive Applications¹

Carbon nanotubes were shown in the last years as attractive nanofillers for polymers in order to reach conductivity at low loadings, enhance mechanical strength and to influence the thermal conductivity, thermal expansion, wear and friction behavior favorably. Most investigations were done on thermoplastic polymers and epoxy compositions. However, also for thermoplastic elastomers, the addition of carbon nanotubes may be a way to replace carbon black and to achieve, at the same time, a better property balance of the nanocomposites. The very low nanotube loadings needed for electrical dissipative or conductive behavior enable enhanced processability, higher surface gloss and even enhanced mechanical strength of the composites as compared to carbon black.

For thermoplastic polyurethanes (TPU), the potential of carbon nanostructures to enhance mechanical behavior was shown by several authors using in solution mixed composites (Koerner and Vaia et al. [1–3], Cho et al. [4], Chen and Tao [5]) or in-situ polymerization in presence of nanotubes or functionalized SWNT or MWNT (Xia and Song [6,7], Jung et al. [8]). In contrast, not much is known about melt mixing of carbon nanotubes into thermoplastic polyurethanes (Jung and Cho [9]). However, for industrial applications for electrical dissipative or conductive composites, i.e. for cables, tubes, belts, shoes, housings etc., melt processing is often the method of choice.

In this paper, different kinds of multiwalled carbon nanotubes (MWNT) were incorporated into Elastollan 1185A using melt processing. For comparison, two types of carbon black were used. The focus of the study is on electrical volume resistivity and changes in tensile test behavior.

Materials and nanocomposite preparation

For this study, TPU Elastollan 1185 A10 was used as granules, if not otherwise mentioned.

As CNT material, different MWNT from Nanocyl S.A. (Sambreville, Belgium, www.nanocyl.com) were used in powdery shape. MWNT1 are very thin straight and coiled nanotubes with a purity >95% (purified MWNT) and MWNT2 are the same nanotubes without purification, having a purity of >60% (crude MWNT). According to Nanocyl S.A. the inner diameters range from 2-7 nm with a mean value of 4 nm and the outer diameters range from 3-15 nm with a mean diameter of 10 nm. The length is up to 50 µm in the as delivered material. In addition, the now industrial available MWNT material Nanocyl 7000 (MWNT3) was tested. This material is an unpurified material having an average diameter of 10 nm, length between 0.1 and 10 µm, and a carbon purity >90% containing up to 10 wt% of metal oxide impurities remaining for the catalyst. The MWNTs are produced via catalytic carbon vapor deposition (CCVD) process.

For comparison, two different carbon blacks (CB) were used. CB1 is Vulcan XC72 from Cabot Corporation (USA). The primary parti-

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¹ Presented at the 7th Fall-Rubber-Colloquium, Hannover, Germany, November 2006

cles in the size of about 30 nm show isolated compact structures of high apparent density without branches as typical for a less structured CB [10]. This material has been the industry standard for imparting electrical conductivity in plastics for many years. As CB2 Printex XE2 (CB) from Degussa was used. This CB is reported to be the best conductive industrially available CB. The primary particles in the size of about 70 nm show structures formed by long branches of particles with a low apparent density and high porosity characteristic of a high structured CB [10].

The materials were properly dried before use. TPU was put in an oven for at least 3 h at 100 °C, whereas the Carbon material were dried at least for 4 h at 100 °C in vacuum. The mixing was performed in two sets. For the first set (set 1) a DACA Microcompounder (DACA-Instruments, Goleta, USA) was used to test the MWNT materials. This microcompounder consists of two conical corotating screws with a bypass allowing the material to circulate for certain time. The DACA was run at 210 °C preset temperature, 50 rpm for 5 min using 4.2 g material input. TPU and MWNT1, MWNT2, and CB1, respectively were fed alternating in 4 parts each. After finishing mixing, the material was led out using the set speed as a continuous strand of about 2 mm diameter. These strands were used directly for electrical measurements. In addition, a premixture of TPU with 15 wt% of MWNT1 and MWNT3 was prepared under the conditions named before which afterwards was diluted with TPU granules in a second step. For comparison, also a masterbatch with CB2 was produced and diluted in the same manner. For the masterbatch dilution, the extruded masterbatch strand was cut in granule size small pieces and a premixture of both granules was fed to the compounder.

In a second set (set 2) an upscaling towards a laboratory extruder was performed. A masterbatch containing 15 wt% MWNT1 was prepared using a Brabender Plast-Corder measuring extruder PL19 (Brabender GmbH & Co. KG, Duisburg, Germany, L=19, L/D=25, 3 – area screw, round shape nozzle) at a rotational speed of 50 rpm and 190–200 °C housing temperatures. The TPU granules were transferred into a powdery shape by cold milling using liquid nitrogen in order to enable an intense premixing of the powdery filler in this concentrate. Of the masterbatch, 300 g were prepared using MWNT1 for which a new batch was ordered from Nanocyl S.A. In a second step the masterbatch was diluted with TPU again in 300 g charges using the same conditions as

for the masterbatch production. After again drying the granules they were injection molded into S2 bars using an Engel ES 200 H machine according to conditions as common for TPU. The bars were annealed at 100 °C for 20 h.

Characterization methods

Electrical volume resistivity was measured directly on the extruded strands of set 1 using an 8002A High Resistance Test Fixture (Keithley) combined with DMM 2000 or 6517A from Keithley. The length between the electrodes was 60 mm, the strand thickness about 2 mm and 3 strands were measured for each sample. For the composites prepared using the Brabender extruder (set 2), the extruded strand thickness reached about 2.5 mm being too thick to be measured by this equipment. The direct measurement of the middle part of the S2 dogbones using the 8002A High Resistance Test Fixture with special clamps for bars led to values out of the measurement range of the electrometer, whereas contact problems may play a role. Thus, middle parts of S2 bars as well as extruded granules were pressed into thin sheets (thickness 0.35 mm, diameter about 60 mm) using a LaboPress 200 at 210 °C. On these samples dielectric measurements were performed at room temperature in a frequency range from 10^{-3} to 10^7 Hz using a frequency response analysis system consisting of Solartron SI1260 Impedance/Gain Phase Analyzer and Novocontrol broadband dielectric converter with the BDC active sample cell (method see [11]). The sheets as well as the strands were cleaned with ethanol before measuring. The stress-strain measurements were performed according to ISO 527-2/5A/20 using a Zwick 1456 machine with pneumatic sample holders and the use of a multisens

adapter for measuring of sample elongation on annealed S2- injection molded bars with a testing velocity of 50 mm/min. The elastic modulus was determined between 0.05 and 0.25 % elongation using 1 mm/min test velocity, a pretension of 0.1 MPa was set. In the figures, characteristic mean curves and mean values of eight measurements are shown.

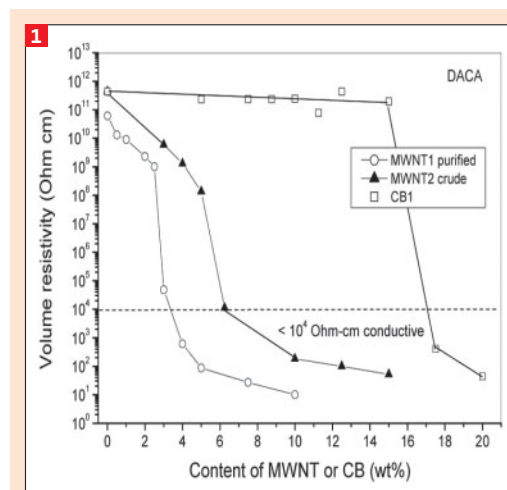
Differential scanning calorimetry (DSC) was performed using a DSC Q 1000 from TA Instruments in the temperature range between –80 °C and 280 °C under nitrogen gas. The first and second heating was performed with a rate of 40 K/min, whereas cooling after holding the sample at 280 °C for 30 s was performed using 10 K/min. Thermogravimetric investigations (TGA) were performed using a TGA7 instrument from Perkin Elmer using the Pyris software version 4.01 in the temperature range between 40 and 700 °C in nitrogen gas with a heating rate of 10 K/min.

Atomic force microscopy (AFM) was done in the tapping mode by a Dimension 3100 NanoScope III (Veeco, USA) on flat surfaces cryocut from extruded strands. The phase contrast images are shown.

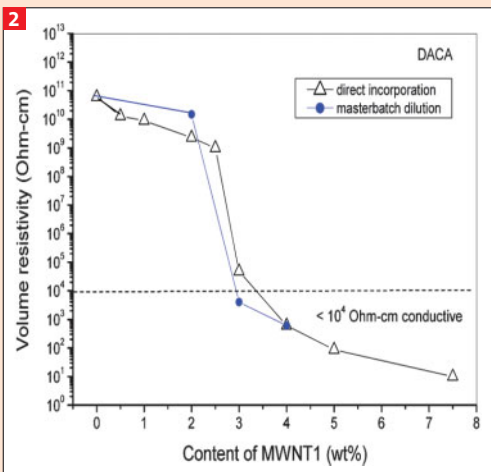
Results

Composites prepared in the DACA microcompounder

The aim of adding carbon nanotubes to TPU was mainly to obtain composites with a certain volume resistivity for antistatic or electrically conductive applications. For basic investigations and the comparison of different kinds of MWNT and CB the DACA microcompounder was used in the first set. Figure 1 shows the volume resistivity of samples of set 1 using the different materials from Nanocyl and CB1 prepared by direct



1 Electrical volume resistivity of TPU-MWNT composite strands prepared using DACA-Microcompounder by direct incorporation

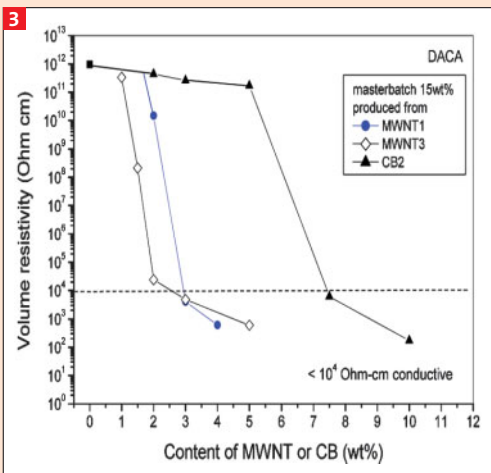


2 Electrical volume resistivity of TPU-MWNT composite strands prepared using DACA-Microcompounder by direct incorporation and masterbatch dilution

For industrial use, the application of masterbatches containing the nanotubes in a polymer bounded form is more favorable. Therefore, different masterbatches were produced and tested. First, the direct incorporation of MWNT1 and the use of a masterbatch containing 15 wt% of MWNT1 was compared as shown in Figure 2.

The comparison shows that in the case of masterbatch dilution slightly lower resistivity values are reached at 3 wt% MWNT1.

Figure 3 compares composites prepared starting from premade masterbatches containing 15 wt% MWNT1, MWNT3, and CB2, respectively. It is clearly seen that the percolation threshold in case of CB2 is much higher than for all MWNT investigated. Percolation was observed between 5 and 7.5 wt%, whereas the composite with 7.5 wt% is electrically conductive. CB2 has much lower percolation composition than CB1 although the incorporation method is not directly comparable. The industrially available product MWNT3 shows a lower percolation composition as compared to MWNT1, even if the purity is lower. This may be explained by a better dispersion ability of these nanotubes as compared to purified materials which have much higher interactions between the tubes themselves (see [12]). At higher loadings the resistivity of the purified sample gets lower.



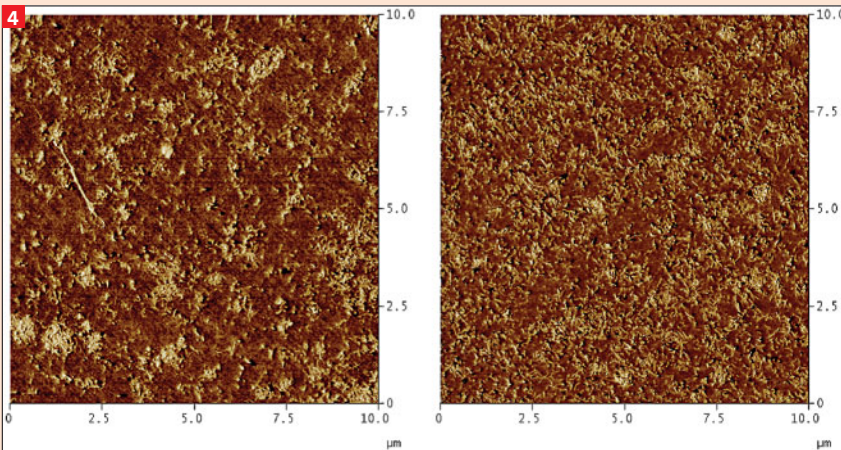
3 Electrical volume resistivity of TPU composite strands prepared using masterbatch dilution by DACA-Microcompounder

incorporation of nanofillers in the TPU matrix. Comparing MWNT1 and MWNT2 it is clearly seen that the purification leads to a lower percolation composition. For the purified MWNT1 material, the percolation starts between 2.5 and 3 wt% whereas for the crude material MWNT2 between 5 and

6 wt%. The samples can be regarded to be electrical conductive (volume resistivity $< 10^4 \text{ Ohm cm}$) starting at 4 wt% MWNT1 and 6 wt% MWNT2, respectively. CB1 shows percolation between 15 and 17.5 wt% addition, which is in accordance with the values given in the data sheet published by Cabot.

Microscopic investigations using AFM are shown in Figure 4. It is clearly seen on these 5 wt% samples that the MWNT dispersion is much better in composites with MWNT3 prepared using masterbatch dilution as compared to composites with MWNT1 directly incorporated. This may be mainly explained by the better dispersability of the as produced MWNT3 as compared to the purified MWNT1 material.

In summary, the electrical measurements showed that the percolation composition in



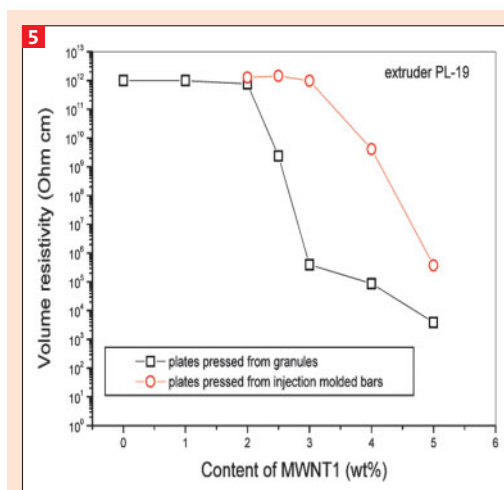
4 AFM images of composites with 5 wt% MWNT1 via direct incorporation (left) and with 5 wt% MWNT3 via masterbatch dilution (right).

TPU based nanocomposite extruded strands lies between 2 and 3 wt% MWNT and depends on the purity and dispersability of the nanotube material. The use of a premade masterbatch leads to slightly lower resistivity near the percolation composition.

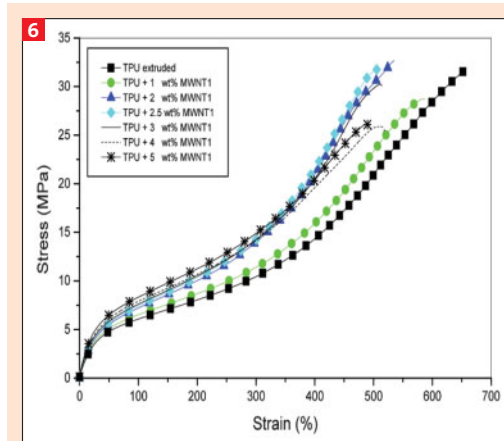
Composites prepared in the laboratory extruder

According to the results of set 1, set 2 was prepared using MWNT1 and masterbatch dilution whereas the laboratory extruder PL-19 was used. Electrical results were obtained from dielectrical measurements on sheets pressed from either the extruded granules or the injection molded samples (Fig. 5).

Unexpectedly, the results differ for both processing states indicating structural differences. The electrical percolation occurs between 2.5 and 3 wt% MWNT1 in case of plates pressed from extruded material, but is shifted to higher concentrations, between 4 and 5 wt%, in plates prepared from injection molded bars. The percolation composition found for extruded material is comparable with the investigations from the DACA Microcompounder, whereas the resistivity values are lower in case of the DACA extruded strands. To explain this quantitative difference, it has to be mentioned that for this set a new lot of MWNT1 was ordered. Comparison of electrical volume resistivity of extruded strands with 4 wt% had indicated that the new lot resulted in slightly higher resistivity values. However, the significant difference between the different processing states of extrusion and injection molding is of quite big interest. Investigations of the influence of injection molding conditions on skin layer formation and orientation of nanotubes in injection molded parts are in progress. Primarily results indicate a strong influence especially of mass temperature and injection speed on the orientation of the nano-



5 Electrical volume resistivity of TPU composites prepared using masterbatch dilution by DACA-Microcompounder



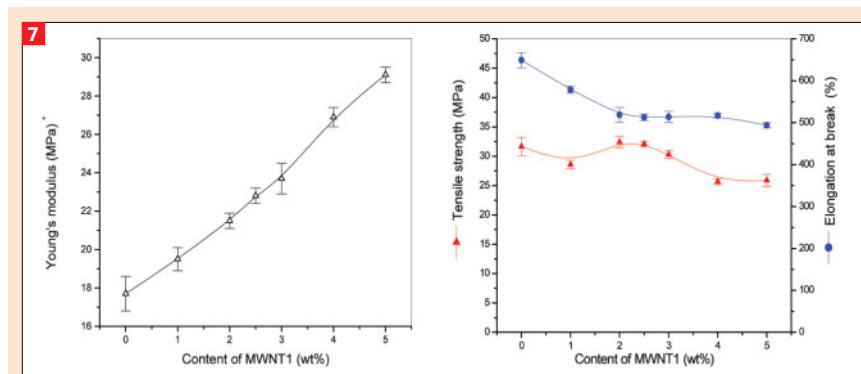
6 Stress-strain curves of TPU-MWNT1 composites prepared using masterbatch dilution by extrusion

tubes and, thus, on the resistivity by some orders of magnitude. This may lead to the conclusion that injection molding conditions have to be adapted in such nanocomposites.

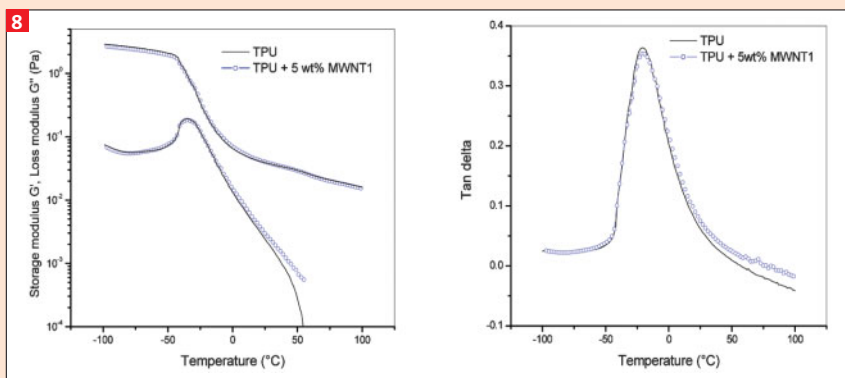
On the samples of set 2 tensile testing was performed. TPU is a thermoplastic elastomer showing high elongation at break. The soft segments act as matrix and provide deformability whereas the hard segment crystals enable melting of the material. It is the aim of adding conductive filler

to remain the elastic behavior of TPU, i.e. not to reduce deformability too much. Figure 6 shows typical stress strain curves of the injection molded samples, whereas Figure 7 displays typical values of the stress-strain-curve.

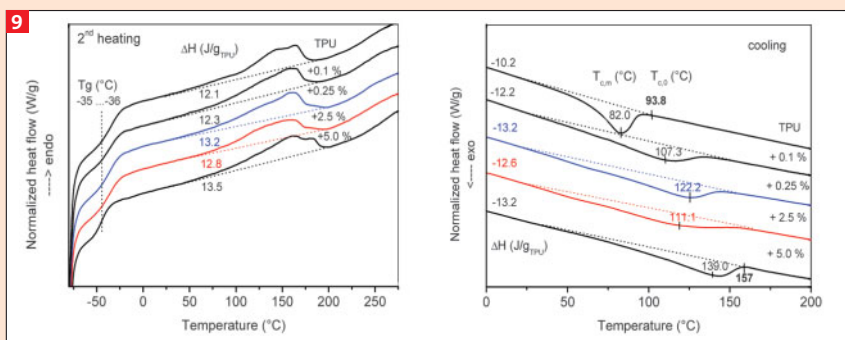
It can be seen that the addition of MWNT1 enhances the Young's modulus linearly and stiffens the sample. Nevertheless, the elongation at break is still as high as 500% showing that the typical mechanical behavior is preserved after nanotube in-



7 Characteristic values from the stress-strain curves shown in Fig.3 for TPU-MWNT1 composites prepared using masterbatch dilution by extrusion



8 Dynamic-mechanical behaviour of TPU-MWNT1 composites prepared using masterbatch dilution by extrusion



9 Second heating and cooling runs of TPU-MWNT1 composites prepared using DACA-Microcompounder by direct incorporation

corporation. For the samples with 4 and 5 wt% MWNT1, which showed reduced resistivity values, the stress values at higher strains are lower than those of the samples filled with 2 and 2.5 wt% indicating the influence of the developing MWNT network like structure within the TPU matrix.

Dynamic mechanical analysis on the middle parts of the injection molded bars was used in order to look at changes in the relaxation behavior of the TPU matrix caused by MWNT addition. Neither the storage modulus, nor the loss modulus or the loss factor are influenced significantly after 5 wt% MWNT addition indicating that the microphase separation is not changed much (Fig. 8). At higher temperatures the

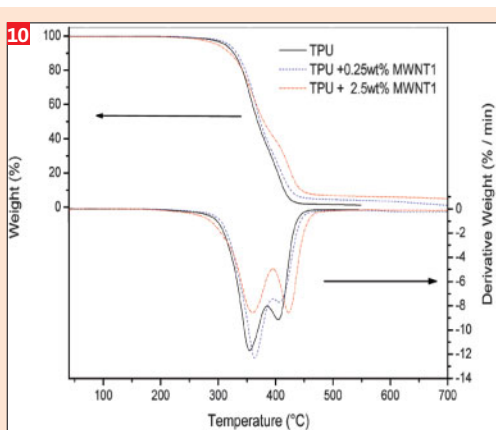
loss modulus and loss factor of the filled TPU is slightly higher than those of TPU indicating the stiffening effect of the MWNT.

Melting and crystallization behavior and thermal stability

It is known and was shown in other systems, that nanofillers can influence the crystallinity and the crystallization behavior of the matrix material. Coleman et al. [13] reported that enhanced crystallinity in poly (vinyl alcohol) / MWNT composites is the main reason for enhanced mechanical properties. In addition, MWNT can act as nuclei shifting the crystallization temperature to higher values. Therefore, also for these composites

the crystallization and melting behavior was studied. In order to see the effect of low loadings, in addition composites with 0.1 and 0.25 wt% MWNT1 were produced using the DACA Microcompounder.

Figure 9 shows the normalized heat flow for selected compositions. It is clearly seen that the addition of nanotubes does not influence the melting behavior very much. The melt enthalpy is only slightly enhanced as compared to unfilled compounded TPU. The glass transition temperature of the TPU soft segments T_g is also not influenced notably. However, the crystallization behavior is changed significantly. After addition of only 0.1 wt% MWNT1 the onset temperature of crystallization $T_{c,0}$ and the maximum crystallization temperature $T_{c,m}$ are shifted by 42K and 25K, respectively. At this low composition we may assume a good dispersion of the nanotubes, thus, each nanotube should be able to nucleate crystallization. At 5 wt% MWNT, where some agglomeration of nanotubes was found, and thus the increase in available surface is not scaled with the amount, we find an increase in $T_{c,0}$ and $T_{c,m}$ by 63K and 57K, respectively. The crystallization enthalpy is slight enhanced indicating higher crystallinity of the hard segments induced by the nanotubes. The same tendencies and relative changes were obtained when comparing the injection molded sample containing 5 wt% MWNT1



10 Thermogravimetry of TPU-MWNT1 composites prepared using DACA-Microcompounder by direct incorporation

and the corresponding TPU sample indicating that the effects also are present in the injection molded samples as used for mechanical testing.

Thermogravimetric investigations (Fig. 10) indicate an enhancement in thermal stability already at low MWNT1 contents.

Summary

It could be shown that carbon nanotubes are effective fillers for TPU in order to get electrically dissipative or conductive composites. Using small scale melt mixing, electrical percolation of as extruded strands could be reached at concentrations as low as 1.5 wt% (< 1 vol%). Electrically conductive composites were obtained starting at 2 wt% addition of Nanocyl 7000 industrial grade material which has an excellent dispersability and led to quite homogeneous dispersion as illustrated by AFM. Direct MWNT incorporation compared to premanufacturing masterbatches having 15 wt% MWNT indicated lower resistivity values in the latter case, which can be related to a more homogeneous MWNT dispersion. Carbon blacks show much higher electrical percolation compositions, as high as 17.5 wt% for Vulcan XC72 and 7.5 wt% for Printex XE2. DSC investigation indicated that the MWNT act as nucleating agents and enhances $T_{c,0}$ and $T_{c,m}$, which may be favorable in processing. In addition, crystallization enthalpy is enhanced. The melting behavior of the hard segments and the glass transition temperature of the soft segments are not influenced much.

In composites prepared by extrusion and injection molding, electrical percolation was found at higher MWNT loadings as compared to compounded strands prepared by the microcompounder. This may be related to different MWNT lots, higher nanotube orientation and alignment, worse nanotube dispersion or breaking of nanotubes during the processing steps. The processes taking place in such nanocomposites during injection molding are not well understood yet.

The excellent mechanical properties of TPU, especially the high deformability, can be preserved in the nanocomposite. Modulus and stress at a given strain are enhanced upon addition of MWNT which may be a combined effect of MWNT incorporation and the slightly enhanced crystallinity.

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