Application of nitrogen doped bamboo-like carbon nanotube for development of electrically conductive lubricants

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Aim of this work was to examine the applicability of nitrogen-doped bamboo-shaped carbon nanotubes (BCNTs) as conductive additive in bearing grease. To synthesize BCNTs, catalytic chemical vapour deposition (CCVD) method was used by applying butylamine as nitrogen containing carbon source. During the preparation of the polydimethylsiloxane (PDMS)-based lubricants BCNT (1.5 wt% or 3 wt%) and Li-soap (5 wt% or 10 wt%, lithium-stearate) or colloidal silicon dioxide (1 wt% and 1.5 wt% Aerosil 200) was added and mixed by using a highly efficient ultrasonic technique. By adding lithium-soap to the BCNT loaded greases their lubricity improved. The electrical conductivity of greases was measured in stationary state and in rotating bearing (during operation) by using an in-house developed instrument. The nanotube containing samples have shown good electrical conductivity (7–18.5 mS). The friction torque was also calculated based on the measurements of our in-house developed instrument. Efficient friction has been achieved with the 1.5 wt% BCNT loaded samples (6.1 and 5.1 Nmm). Thus, small amount of BCNT is enough to develop a conductive grease formula. All in all, the 3% BCNT and 1.0% colloidal SiO2 containing PDMS base-oil with 50 mm/s viscosity is well suitable for loading of ball bearings.

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1. Introduction

Electric motors are more and more widespread, therefore, problems related to their operation, such as electrical discharges in the ball bearings, are becoming increasingly prevalent. The generated electric sparks can cause damage by melting some points of the metal-surfaces in the bearing, which lead to uneven raceways, and the early degradation of bearings [1]. This problem can be avoided by applying electrically conductive lubricants. Nowadays, various conductive components are used in the greases such as ionic liquids, copper, silver, carbon black and graphite [2–4]. Zhang et al. used reduced graphene oxide in hyperbranched polyamine-ester base oil and thus, achieved a solvent-free novel lubricant [5]. Several complex, carbon based electrically conductive materials have been intensively applied as nano-additives in conductive greases, including nanosized Al coated graphene, nanosilver-polydopamine coated carbon nanospheres, NiCo layered double hydroxides/graphene oxide, graphene/lanthanum oxide KOH/N-graphene [6–10]. The surface polarity and the particle size of the conductive additives will influence the homogeneity and stability of the produced greases. Highly homogenous dispersibility can be achieved in the base-oils by using nanosized conductive materials as additives. Carbon nanotubes are remarkably electrically conductive nanostructured materials [11]. Their electronic properties can be tuned by incorporating nitrogen atoms (doping) into the graphitic structure of nanotube sidewalls [12–14]. The N-doped carbon materials are well suited in various systems, such as lithium ion batteries, fluorescent bioimaging, and supercapacitors [15–17]. Nitrogen doping can easily be accomplished by using nitrogen containing carbon sources (amines) in the CCVD (catalytic chemical vapour deposition) synthesis of nanotubes [18–22]. Four types of nitrogen can be found in the N-doped carbon nanotubes: pyridinic, pyrrolic, quaternary and oxidized pyridinic [23]. The structure of the nanotubes is also affected by the nitrogen incorporation which will lead to the formation of the so-called N-doped bamboo-shaped carbon nanotubes (BCNTs) [13]. Nitrogen-doped BCNTs have been characterized by scanning tunneling spectroscopy [24]. By comparing the tunneling spectra of multi-walled carbon nanotubes (MWCNTs) and N-doped BCNTs, it can be seen that the nitrogen-doped system has an additional electronic feature at ~0.18 eV, while in case of the MWCNTs the valence and conduction band appear symmetric about the Fermi level. It can be also noted that the presence of an electronic density of states (DOS) at the Fermi energy indicates that the electronic features of N-doped materials is similar to metals [15,25–27]. The degree of electrical conductivity of BCNTs can be tuned within wide range by modifying the nitrogen content [28,29]. The amount of incorporated nitrogen atoms can be increased by adjusting the CCVD synthesis parameters (e.g. temperature, type of carbon source, catalyst). Increasing synthesis temperature will lead to decreasing nitrogen content [30]. The electronic conductivity of BCNTs is highly depend on the amount of incorporated nitrogen atoms, in this sense their conductivity is customizable by varying the synthesis temperature [31]. Another advantage of the N-doped BCNTs is their oxidizable structure. Nitrogen-doped BCNTs contain several carboxyl and hydroxyl groups on their walls. Due to the above-mentioned remarkable properties of the BCNTs, are promising conductive additives for grease. Hydrogen bonds, secondary oxygen bridges and other interactions can be formed between the CNT filler and the base oil [32,33]. Thus, CNTs are well connected to the structure of the base oil creating a stable dispersion, and homogeneous grease.

2. Experimental

2.1. Materials

Nitrogen doped carbon nanotubes were synthesized by applying butylamine (C₆H₁₃N, Merck) as carbon source, nickel(II)-nitrate hexahydrate (Ni(NO₃)₂ × 6H₂O, Aldrich) and magnesium oxide (MgO, Reanal) as catalysts for the CCVD process, nitrogen (Messer, 99.995%) was used as carrier gas. Silicone oils with 5000 mm/s and 50 mm/s viscosity, lithium-stearate (C₁₈H₃₇LiO₂, Aldrich) and colloidal silicon dioxide (Aerosil 200, Sigma Aldrich) were used as base-oil, soap and thickener additive of greases, respectively.

2.2. Methods

2.2.1. CCVD synthesis of the BCNTs

The synthesis of BCNTs was carried out by using the Catalytic Chemical Vapour Deposition (CCVD) method using a previously optimized synthetic procedure [20]. Nickel containing (5 wt%) magnesium oxide (2.00 g) was placed into a quartz reactor in tube furnace, which was heated up to 750 °C temperature. The synthesis time was 20 min within which the carbon source (butylamine) was dosed by a syringe pump (6 ml h⁻¹) into the reactor and vaporized to carry onto the catalyst bed by nitrogen (100 ml min⁻¹). The cycle was repeated 20 times. The nickel containing catalyst was removed by hydrochloride acid from the nanotubes. The purity of BCNTs was confirmed by thermogravimetric analysis and the carbon content was found to be 95.6%.

2.2.2. Preparation of BCNT containing conductive bearing greases

Conductive greases were produced by high energy ultrasound technology. Carbon nanotubes were dispersed in polydimethylsiloxane by using Hielscher UIP1000hd tip homogenizer (340 W/19.42 kHz, 2 min) from Hielscher Ultrasounds GmbH. Ultrasonic cavitation leads to homogenous greases with great stability. The highly intensive sonication of greases results alternating high-pressure and low-pressure cycles in the base-oils. During the low-pressure cycle, small vacuum bubbles are forming in the liquid. The volume of the bubbles will reach a maximum where they cannot absorb more energy and collapse during the high-pressure cycle. At the point of collapse, very high temperatures (∼5000 K) and pressures (∼2000 atm) are reached locally. The cavitation can be achieved in liquid phase jets (up to 280 m/s velocity), which is more than enough to produce very homogenous and stable greases. The total weight of the grease samples was 100 g, within which silicone oil (polydimethylsiloxane, PDMS) was
used as basic component. The BCNT content was 1.5 wt% or 3 wt%, while as soap to increase the lubricity of the samples, 5% or 10% of lithium-stearate was applied. The colloidal silicon dioxide containing samples were prepared by using 1.5 wt% or 3 wt% BCNT, 1.5 wt% or 2.5 wt % SiO2 (Aerosil), while the base oil was Wacker 5000 silicone oil (viscosity: 5000 mm/s).

2.2.3. Characterization techniques
Morphology, diameters and structure of the BCNTs were studied by FEI Technai G2-20X Twin high-resolution transmission electron-microscopy (HRTEM) operating at an accelerating voltage of 200 kV and Philips CM 10 (100 kV) transmission electron-microscopy (TEM). The purity (carbon content) of the carbon nanotube sample was measured by thermogravimetric analysis (TGA), by using of Netzsch Tarsus TG 209 thermo-microbalance. Nitrogen (4.5) and oxygen (5.0) mixture was applied as oxidative atmosphere in the TGA measurements. The flow rate was set to 6 ml min\(^{-1}\) and 14 ml min\(^{-1}\), for the oxygen and nitrogen, respectively. The heating rate was 10 °C min\(^{-1}\), in the 35–800 °C temperature range. The sample preparation was carried out by drying from aqueous suspension of the samples onto a copper grid (300 Mesh, only carbon from Ted Pella). The binding-type of incorporated nitrogen atoms was studied by SPECS X-ray photoelectron spectroscopy (XPS) with Phoibus 150 MCD nine analyzer.

The frictional properties of carbon nanotube loaded bearing grease were measured by a Basalt-NZ equipment, where Cr6 steel plate and a steel cylinder with 6 mm diameter and 16 mm length was used as substrate and counter material. During the measurement 250 cycles was performed at room temperature by applying 5 N load, 60 MPa contact pressure and 20 mm/s maximum sliding speed. The applied load (Fn), and tangential force (Ft) was used to calculate the coefficient of friction by using an Ft/Fn formula.

The dropping points of the greases were measured based on the ASTM D566 – 17 standard. The test tube was placed in a silicone oil bath which was heated at a rate of 5–6 °C per minute, while being stirred.

The electrical conductivity was determined in stationary state by applying Orion Versa Star Pro conductivity meter (Thermo Scientific).

For the friction and electrical conductivity measurements, 100 mg grease sample was loaded in single row radial ball bearing (608 LBiN; OD: 22 mm). The conductivity of greases in the ball bearings during operation was determined at 2000 min\(^{-1}\) rotational speed by using an in-house developed system (Fig. 1).

A CompactRIO (NI cRIO-9031) was used to control the measurement procedure. The system is equipped with a constant current source (NI-9265), a high precision digital input module (NI-9219) and a digital I/O module (NI-9403). The procedure was carried out by using a pair of bearings (608LB). The original lubricant was replaced with the tested mixture, using a new pair of bearings for each test.

A rotary encoder is used to measure the rotation speed of the DC motor, which is controlled through power electronics. A fan wheel is attached to the motor to simulate real world load scenarios. The measurement process is automated, it can be done at specific speed(s) manually.

Fig. 1 – In-house developed system to determine electrical conductivity and torque friction of greases in ball bearings.

The system used 4-wire measurement method. The source drives constant current (10 mA by default, can be modified by the user) through the bearings and measures the voltage drop on them. The controller calculates the resistance of the bearings and displays it on a graph and saving the data at the same time. Measurements are done continuously for 5 s, calculating average, minimum and maximum values for resistance.

In order to determine the lubrication and the applicability of BCNT loaded grease in ball bearing friction torque (M\(_\text{d}\)) was calculated based on the free rotation time of a steel flywheel after switching off the engine (Eq. (1)):

\[
M_d = 0.7 \times 10^{-3} \times \omega/t_d
\]

where \(t_d\) was the free rotation time of the flywheel, \(\omega\) was the angular speed (rotational-speed \(\times 2\pi\)). The mass moment of inertia of the flywheel, which also includes the inertia of the silicone shield of the ball bearing is \(0.7 \times 10^{-3}\) kg m\(^2\). The rotational-speed during the tests was set to 33.33 s\(^{-1}\) (2000 min\(^{-1}\)). Polydimethylenesiloxane based bearing grease, one of the most widely employed non-conductive lubricant, was used as reference and its friction torque was measured (4.9 Nmm) for comparative purposes.

3. Results and discussion

3.1. Characterization of BCNTs

The purified nitrogen doped carbon nanotubes were examined by transmission electron microscopy (Fig. 2a). On the TEM picture were not visible impurities, which origin from the CCVD catalyst, and the sample not included amorphous carbon forms. Diameter of nanotubes were measured by applying of ImageJ software, based on the scalebar of TEM picture. The outer diameters of BCNTs were measured between 8 and 44 nm, the average diameter was 18.8 ± 7.4 nm (Fig. 2b). The purity, namely the carbon content of the purified BCNT sample was 92.6%, based on the thermogravimetric analysis (Fig. 2c).

The bamboo-shaped structure of the BCNTs is visible on the HRTEM images (Fig. 3a). The average diameter of the carbon nanotubes was 18.5 nm. The schematic illustration of the bamboo-like structure also shows several edges on the wall of nanotubes (Fig. 3b). In the synthetized BCNTs, based on the deconvoluted N 1s band of the XPS spectrum, three types
of nitrogen atom can be differentiated: pyridinic, graphitic (quaternary) and oxidized nitrogen with a binding energy at 398.5 eV, 401.1 eV and 404.9 eV, respectively (Fig. 3c). The incorporation of these nitrogen atoms into the system will led to structural distortion (bamboo-shape, edges) and electronic property change. The formed edges can serve as adsorption sites for base-oil molecules and soaps, which will enhance the dispersion stability of BCNT containing grease.

3.2. Coefficients of frictions of BCNT loaded greases

In case of the soap-free greases the loading of BCNTs lead to increasing coefficients of friction (Fig. 4). Thus, to achieve proper lubrication Li-soap has to be used in the samples. The nanotube free soap containing lubricants has similar degree of friction as the BCNT contained samples. The coefficients of friction were very similar in case of the four BCNT and Li-soap contained greases.

3.3. Tests of the greases

Due to the area of applications (in ball bearings) of the prepared greases, it is necessary to reach high dropping point (>140 °C) during operation. The dropping points were measured based on the ASTM D566 – 17 standard. By using BCNT as additive in the samples, the dropping point decreased, therefore, new composition was made. In order to improve the dropping points, high viscosity silicone oil (5000 mm²/s) and fumed silica was used as thickener. These further additives increased the dropping point and it is reached >150 °C (Fig. 5a).

The conductivity of the lithium soap/BCNT and the SiO₂ containing samples was measured in stationary state. It was found to be relatively high, >5 mS in each case (Fig. 5b). The sample with 3% BCNT/5% Li-soap has a ~9 mS conductivity in stationary state. The 1.5 wt% BCNT containing silica aerogel filled grease showed the smallest electrical conductivity in stationary state. In case of the 3% nanotube/silica loaded grease reached 4.5 mS conductivity, which was higher than in the previous case.

The electrical conductivity was also measured during operation of the ball bearing (Fig. 5c). The conductivity increased in each case compare to the stationary state measurements. The maximum (31.5 mS) was reached with the 3% BCNT containing, silica loaded lubricant. By increasing amount of Li-stearate the conductivity of the four samples decreased; thus, it is necessary to optimize the amount of the soap. Friction torque was measured during the operation of the bearing with the selected lubricants (Fig. 5d). The 3% BCNT containing samples are good conductive greases, but their friction torque is higher (14.2 and 16.1 Nmm) than the 1.5% nanotube loaded samples (6.1 and 5.2 Nmm). The 1.5% BCNT samples are similar to the non-conductive reference bearing grease in terms of friction torque (4.9 Nmm). The SiO₂ filled lubricants showed relative high friction torque, 12 and 13.6 Nmm. The sample which contain 1.5% BCNT and 5% soap can be a perfect candidate as conductive bearing grease, but the dropping point is
much lower than expected. All in all, the 3% BCNT and 1.0% \( \text{SiO}_2 \) containing grease was well suitable for loading of ball bearing.

4. Conclusion

High energy ultrasonication was applied to produce homogeneous, stable and electrical-conductive bearing greases. Bamboo-shaped carbon nanotubes (BCNTs) were used as conductive additives for greases. Due to nitrogen incorporation into the structures, extraordinary electronic and structural properties developed which lead to good adsorption behavior and electric conductivity. Relatively small amount of BCNTs, 1.5 wt% is enough to reach good electrical conductivity of greases (>14 mS). The friction torque of the 1.5 wt% nanotube and 5 wt% soap containing conductive grease sample (6.1 Nmm) was similar to the non-conductive grease, which is widely used nowadays for loading of the ball bearings. Dropping points of the soap and BCNT containing samples were very low, thus the composition of the lubricants was modified. By using colloidal silicon dioxide and 3 wt% BCNT in high viscosity (5000 mm/s) silicone oil resulted high dropping point, 153 °C. All of these effects are based on the ability of dispersed silica particles (aerosil) to form a network of aggregates via hydrogen bridges and/or van der Waals interactions in silicone.

Fig. 4 – Coefficients of friction of the prepared lubricant samples.

Fig. 5 – Dropping point (a), electrical conductivity of the lubricants in stationary state (b) and in rotating bearing, during operation (c), friction torque in rotating bearing (d).
oil. The nitrogen atoms and the oxidized functional groups in the added N-doped BCNTs further increase the possibility of interactions. Thus, a reversible, three-dimensional lattice structure could form and the viscosity of the SiO$_2$-PDMS-BCNT will increase. However, the friction coefficient (12 Nmm) was higher than in case of other samples, the electrical conductivity in bearings during operation was 31.5 mS. All in all, the 3% BCNT and 1.0% SiO$_2$ containing grease has the best characteristics to apply in ball bearings. Consequently, BCNT is well suited for the development of a conductive grease formula.

Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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