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Liquid sensing properties of fibres prepared by melt spinning from poly(lactic acid) containing multi-walled carbon nanotubes

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ABSTRACT

Poly(lactic acid) (PLA)/multi-walled carbon nanotube (MWNT) composites were melt spun with different take-up velocities (max. 100 m/min) to obtain electrically conductive fibres. The incorporation of MWNT contents between 0.5 and 5.0 wt.% was realised in a previous melt mixing process using twin-screw extrusion. The relative resistance change of the fibres caused by contact with different solvents (water, *n*-hexane, ethanol, methanol) and solvent concentrations was used as liquid sensing response, whereas the time dependent resistance was recorded during immersion and drying cycles. Transmission electron microscopy and Raman spectroscopy indicated enhanced orientation of MWNT along the fibre axis with take-up velocity, resulting in decreased sensitivity during solvent contact. Additionally, sensitivity decreased as the weight content of MWNT increased and was furthermore dependent on the characteristics of used solvents. In context with the targeted application of leakage detection, fibres with low MWNT amount and low draw down ratio (as extruded fibres with 2 wt.% MWNT) are suitable, as they showed relative resistance changes of up to 87% after 10 min immersion in methanol even if the recovery upon drying was suppressed significantly.

1. Introduction

Besides the exceptional mechanical, thermal, and electrical properties [1–4], the use of carbon nanotubes (CNT) as sensor materials represents an interesting field of research. One scientific field concerns the incorporation of CNT into a polymer matrix to create sensory composite materials. Up to now some work has been done to investigate the possibilities of detecting mechanical strain [5,6], temperature changes [7,8], and different chemicals in form of gases, liquids and vapours [9–13] by means of CNT polymer composites.

Basically, such sensory materials detect changes of environmental conditions, like mechanical strain, temperature, or presence of vapours or liquids, whereas the composites respond with changes of the conductive CNT network. This change of network structure normally goes along with an electrical response, which can be easily measured and analysed.

In case of liquid sensing, solvent sorption leads to swelling of the polymer matrix resulting in a partial disruption of contacts or increase in the distances between neighboured nanotubes above the tunnelling or hopping distances causing a resistance increase. Thus, a good dispersion of the nanotubes and an establishment of a percolated nanotube network within the polymer matrix are preconditions to use a composite for sensing trials. This aim provides a challenge, as nanotubes are produced in agglomerated structures [14,15], which have to be dispersed. For MWNT within PLA we recently successfully optimised melt mixing conditions for preparation and dilution of a masterbatch using a twin-screw extruder in order to achieve a good filler dispersion [16]. For these composites the liquid sensing properties were investigated using compression-moulded plates [17] and aspects of the liquid sensing mechanism were examined [18]. It could be shown that the resistance reversibly changed upon the cycles with good reproducibility. Lower MWNT loadings resulted in larger resistance changes, indicating that the conductive MWNT network tends to readily disconnect due to the less dense structures as compared to higher loadings. Various solvents (*n*-hexane, toluene, chloroform, tetrahydrofuran, dichloromethane, ethanol, and water) were successfully detected, showing different degrees of resistance changes which could be related to the difference in the solubility parameters between PLA and the solvents used.

On the route towards applications in consumer goods reasonable devices have to be manufactured. Beside sensors made of bulk materials the use of fibres is very interesting because they can be used in textiles. Thus, flexible sensors or sensor arrays with large

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dimensions can be processed. However, it is well known that the morphology and thus electrical and sensing properties of CNT polymer composites is strongly related to the processing conditions. Consequently and based on previous work we further investigate the sensing behaviour of PLA/MWNT composites in the form of endless melt spun fibres within the framework of the European project INTELTEX. In a first step the processing conditions to manufacture fibres reasonable for liquid sensing were investigated. In the second step the triangle between processing, morphology, and sensing properties will be discussed.

One of the targeted applications is the use in textiles as applied for coatings in tanks, canisters, or containers in order to detect solvent leakage. Such a textile should contain sensing fibres announcing the occurrence of a leakage and possibly also the location of defects. For this application the main requirement is a fast and significant sensing response.

2. Materials and experimental methods

2.1. Materials and composite preparation

PLA L 9000 from Biomer (Germany) was chosen as matrix polymer. PLA usually hydrolyses at temperatures above glass transition temperature (T_g) of 60 °C and melts at 170 °C. Due to its susceptibility towards water absorption, the pellets were dried in vacuum for 18 h at 40 °C prior every processing step. Furthermore, PLA exhibits a good spinnability where high take-up velocities are achievable [19–21]. In addition, it can be produced from renewable resources and is a biodegradable and compostable "green" polymer [22,23], which makes it interesting for the life-cycle analysis of new potential products.

Nanocyl®-7000 (Nanocyl S.A., Belgium) MWNT were used as filler material. These MWNT are produced by chemical vapour deposition and available in large scales. According to the supplier they have a purity of approximately 90%, an average diameter of 9.5 nm, and an average length of 1.5 μm.

The compounding processes of masterbatch production and dilution were performed using a co-rotating twin-screw extruder ZE25 (Berstorff, Germany) having a screw diameter of 25 mm and a barrel length of 900 mm (L/D = 36). For the masterbatch production PLA pellets and the powdery MWNT material were fed simultaneously into the hopper by gravimetric dosing. For the masterbatch dilution, pellets of the masterbatch and the diluting PLA were premixed. An optimised screw configuration containing mainly mixing elements and several left-handed back pressure elements, a rotations speed of 500 min^{-1}, and a temperature profile ranging from 180 °C to 220 °C were used. More details on processing can be found in [16].

2.2. Melt spinning

PLA composite fibres were melt-spun using a self-constructed piston-type spinning device (Fig. 1), where the granular composite material is molten in a heatable cylinder and pressed through a single hole die of 0.6 mm in diameter by a piston. The volume throughput was controlled by the adjustable piston speed and was kept constant at 0.755 cm^3/min. The melt-spun monofilaments were collected on a winder, whereas the take-up velocity was set to 20, 50, and 100 m/min corresponding to draw down ratios of 7.3, 18.2, and 36.5. Additionally, fibres without using a winder were prepared, which are named as "extruded" in the following. The diameter of the fibres decreased with increasing take-up velocity from 600 μm (extruded) down to 100 μm for fibres drawn with 100 m/min. All spinning trials were performed at 220 °C after melting 10 g of composite material for about 3 min.

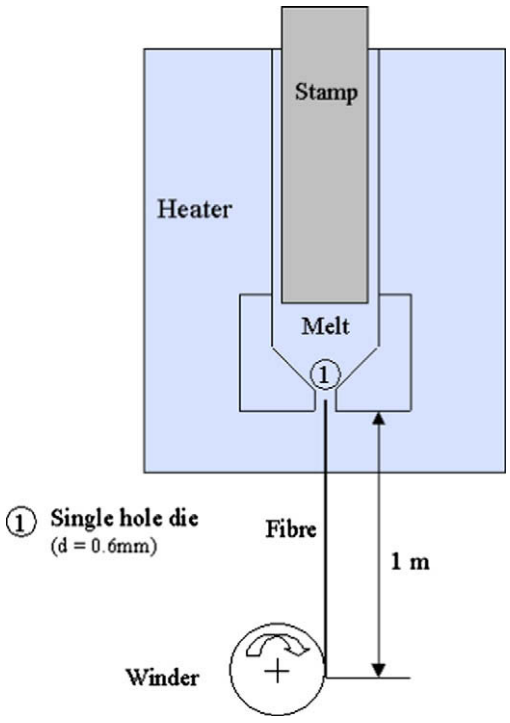

Fig. 1. Piston type spinning device for production of monofilaments.

2.3. Fibre characterisation

2.3.1. Transmission electron microscopy (TEM)

An analytical TEM (EM 912, Zeiss, Germany) was used to investigate the changes in MWNT network formation due to the melt-spinning process. Especially MWNT orientation within the PLA fibres was of interest. The microscope was adjusted with an acceleration voltage of 120 kV, whereas defocusing and use of a zero loss filter led to best filler/matrix contrasts. Small pieces of fibres were embedded in epoxy resin and cut parallel to the fibre direction to obtain thin sections of 150 nm thickness. The cutting was performed using a Reichert Ultracut S ultramicrotome (Leica, Austria) in combination with a diamond knife (Diatome, Switzerland).

2.3.2. Polarised Raman spectroscopy

Polarised Raman spectroscopy was performed to access a quantitative estimation of MWNT orientation, as it was successfully performed in previous studies [24]. The spectra of single fibres, which were fixed on glass slides, were collected using a Raman spectrometer HoloProbe 5000 (KOSI Inc.) equipped with a light microscope (Leica) and a CCD detector. The wavelength region of 150–4000 cm^{-1} was investigated using a laser with a power of 11 mW and a wavelength of 785 nm. One spectrum consisting of 50 scans was recorded with the program HoloGRAMS. The interesting spectral regions near by 1284 and 1609 cm^{-1} for the D and G-band, respectively, were collected with parallel (D_{par}, G_{par}) and perpendicular (D_{perp}, G_{perp}) polarised excitation with respect to the fibre axis. Hereby, the G-band at 1609 cm^{-1} is related to the in-plane vibrations of C–C bonds of the graphitic wall and the D-band at 1284 cm^{-1} can be related to the disorder in the graphitic structure. Calculating the ratios D_{par}/D_{perp} and G_{par}/G_{perp} using the band area of the collected spectra leads to a measure for the MWNT orientation. A statistical failure analysis was performed, whereas the statistical deviation of the measurement signal itself was calculated by using the Gaussian Error Distribution Function.