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Melt- and Wet-Spinning of Graphene-Polymer Nano-Composite Fibres for Multifunctional Textile Applications *

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Abstract

In this work, we report about melt- and wet-spinning of graphene nano-composite fibres with different polymer matrix materials. In case of melt-spinning, the development of a textile supercapacitor with melt-spun polyamide-6 yarns including 1 wt% of graphene is reported. Melt spinning of graphene/polyamide-6 is performed at pilot scale leading with winding velocities of 1,400 m/min. Subsequently, the graphene/polyamide-6 yarns are processed to woven fabrics and transferred into a supercapacitor. Electrical capacities of 1.14 and 1.82 mF/g are achieved for atlas- and plane-weave woven fabrics.

In case of wet-spinning, trials with graphene and polyvinyl alcohol (PVA) and the investigation of the obtained fibres’ properties are reported. By incorporation of 10 wt% of graphene into the polymer material, an increase of the tensile strength about a factor of 10 can be observed. Furthermore, after-treatment steps of drying and drawing are investigated.

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Keywords: Graphene, polyamide 6, melt-spinning, supercapacitor, textiles

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1. Introduction

Graphene, the two-dimensional allotrope of carbon, has attracted tremendous interest of international researchers due to its extraordinary properties. Besides the research on ultrafast- and terahertz electronics, also the fabrication of high-performance composite materials has come into the focus of research interest. Hereby, the development of new-type energy storage devices, i.e. batteries and supercapacitors, is one of the greatest fields of research in graphene. Especially for a new generation of textiles, so called smart textiles, the development of mobile, textile-based power sources is from great importance. Thus, several research papers have been already published in which fibre-based supercapacitors were presented [1-5]. By a wet-spinning approach of neat graphene fibres, electrical capacities up to several 100 F/g were achieved which is significantly higher than the values of commercially available supercapacitors [6]. Several other wet-spinning trials have been published so far, especially by Chao Gao and Aboutalebi et al. in which extraordinary electrical conductivities of more than 10^4 S/m were achieved [7-10]. These conductivities make the fibres attractive as electrode materials in textile supercapacitors. However, currently there isn’t any textile supercapacitor available on the market. One problem of the published research works is the fact that the mass throughput of the fabricated fibres is not high enough for up-scaled integration into textiles as the winding velocities are limited to values below 5 m/min. As a consequence, alternative approaches towards fibre-based energy storage devices have to be developed. Within this work, we present a graphene-modified and melt-spun polyamide-6 textile structure which shows potential for use as electrode material in textile supercapacitors. Despite the lack of the currently low winding velocities of wet-spinning of graphene, first attempts in process development of wet-spun graphene nano-composite fibres are made in order to develop a process window for further, up-scaled wet-spinning experiments.

2. Materials and methods

2.1 Aim of the study

Within this work, we demonstrate the spinnability of graphene-modified polyamide-6 (PA6) multifilament yarns by use of a commercially established melt-spinning process. Furthermore, the aim of this study is to evidence the usability of graphene/PA6 yarns and woven fabrics for use as textile energy storage devices. Therefore, a supercapacitor demonstrator including a current collector and an electrolyte material is manufactured.

In case of wet-spinning, the main goal of this research work is to fabricate graphene-modified polyvinyl alcohole (PVA) fibres within a lab-scale wet-spinning process and to investigate the influence of the graphene addition on the structural and mechanical properties of the obtained fibres. Influence of drawing and drying onto the yarn properties is investigated, too. By use of the obtained process data and the knowledge of the influence of post-treatment steps onto the fibres’ properties, a continuous pilot-scale wet-spinning process of graphene-polymer fibres can be developed thus enabling an up-scaled production of high-performance nano-composite fibres.

2.2 Materials

2.2.1 Melt-spinning

For melt-spinning, polyamide-6 material is purchased from BASF AG, Ludwigshafen, Germany (Ultramid® B24 N03). Graphene platelets are purchased from Avanzare S.A., La Rioja, Spain. In a first step, graphene-polyamide masterbatches with 1 wt% graphene mass loading are prepared by use of a twin-screw compounder of Brabender GmbH & Co. KG, Duisburg, Germany. The as-prepared masterbatches are subsequently melt-spun with the same graphene mass fraction following the procedure described in chapter 2.3.

2.2.2 Wet-spinning

Wet-spinning is performed at laboratory scale with graphene flakes and PVA polymer material. Graphene flakes are provided from Applied Graphene Materials PLC, Cleveland, Great Britain. Determination of aspect ratio of the
graphene flakes is performed via atomic force microscopy. PVA from Sigma Aldrich (363146 Aldrich, M_w = 146–148 MPa, 99% hydrolysed) is used as matrix polymer material. Spinning solutions of graphene/PVA in water are produced with a graphene mass fraction of 10 wt%. As coagulation material, acetone is used.

2.3 Methods

2.3.1 Melt-spinning

In a first step, the graphene/PA6 masterbatches are melt-spun to multifilament yarns by use of a pilot-scale bi-component melt-spinning plant of Fourné Anlagenbau GmbH, Alfter-Impekoven, Germany. The graphene/PA6 material is put into an extrusion line by use of a hopper and subsequently molten in the extruder at 270 °C. The molten polymer is pressed through a spin package consisting of 24 capillary openings leading to multifilament yarns which are bundled by a spin-finish. The obtained yarn is finally drawn at 70 °C and wound onto several pairs of rotating godets with a maximum winding velocity of 1,400 m/min. The applied process parameters are presented in table 1.

<table>
<thead>
<tr>
<th>Process parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extrusion temperature</td>
<td>220-260 °C</td>
</tr>
<tr>
<td>Temperature at spinneret die</td>
<td>250 °C</td>
</tr>
<tr>
<td>Winding velocity</td>
<td>500 – 1400 m/min</td>
</tr>
<tr>
<td>Applied draw ratios</td>
<td>1.1 – 2.0</td>
</tr>
</tbody>
</table>

After melt-spinning, the PA6 yarn containing 1 wt% graphene, is analyzed via microscopy as well as DC electrical conductivity measurements and further processed to woven fabrics including graphene-modified yarns in warp- and weft-direction. A light microscope Leica DN 4000M of Leica Microsystems GmbH, Wetzlar, Germany is used and a LEO 1450 VP of LEO Electron Microscopy Ltd., Cambridge, Great Britain, is used for scanning electron microscopy measurements. Measurement of electrical conductivity is performed with a DC Picoamperemeter 6487/E of Keithley Corp., Solon/OH, United States. Plane-weave woven fabrics are fabricated on an industrial shuttle weaving machine NH-2 of Jakob Müller AG, Frick, Switzerland.

The obtained graphene woven fabrics are finally processed into a textile supercapacitor. Therefore, a nonwoven is soaked with a supersaturated sodium sulfate solution and then connected with the graphene/PA6 woven fabrics which are acting as electrode material. The woven fabrics are finally contacted with aluminium foil which serves as current collector. Discharging curve is recorded by use of an oscilloscope and the resulting discharging curve is used for determination of the resulting specific capacity of the textile supercapacitor.

2.3.2 Wet-spinning

For wet-spinning trials, a lab-scale piston spinning plant is used which is shown in figure 1.
In a first step, a spinning solution of PVA (and PVA/graphene, respectively) is prepared in water at 100 °C under reflux for 8 h. Monofilaments of neat PVA and filaments of PVA with 10 wt% graphene mass loading are spun with a spinneret die diameter of 0.16 mm. The spinning pump is connected to a nitrogen supply thus enabling constant pressure of 5 bar. The acetone coagulation bath is adjusted to a temperature of 15 °C.

Analysis of the obtained filaments is performed via optical- and electron microscopy as well as via tensile tests. A light microscope Leica DN 4000M of Leica Microsystems GmbH, Wetzlar, Germany is used and a LEO 1450 VP of LEO Electron Microscopy Ltd., Cambridge, Great Britain, is used for scanning electron microscopy measurements. Mechanical properties are analyzed with a tensile testing device Z2.5 of Zwick GmbH & Co. KG, Ulm, Germany. Tensile tests are performed in accordance to DIN EN ISO 2062.

The spinning parameters are summarized in table 2.

Table 2. Overview of wet-spinning parameters.

<table>
<thead>
<tr>
<th>Spinning parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinning solution</td>
<td>PVA and PVA with 10 wt% graphene</td>
</tr>
<tr>
<td></td>
<td>Stirring for 8 h at 100 °C</td>
</tr>
<tr>
<td>Spinneret die diameter</td>
<td>0.16 mm</td>
</tr>
<tr>
<td>Coagulation bath</td>
<td>Acetone at 15 °C</td>
</tr>
<tr>
<td>Applied pressure</td>
<td>5 bar</td>
</tr>
</tbody>
</table>

For further processing, drawing and drying steps are applied. In a first step, the filaments are dried whereby drying is performed via hot quench air or alternatively in a desiccator device. Air-drying is performed at 50 °C for 10 minutes. Desiccator-based drying is performed in a vacuum atmosphere for seven days. Phosphorous pentoxide is put into the desiccator as drying agent. Subsequent drawing is performed either via thermal drawing by use of two heating godets operating at 100 °C, or alternatively via wet-drawing whereby the filaments are put at first into an acetone-water solution with volume ratio of 1:1 and subsequently drawn with rotating godets. In both cases, a draw ratio of 1.3 is applied. The post-treatment steps are summarized in table 3.
Table 3. Post-treatment steps

<table>
<thead>
<tr>
<th>Applied steps</th>
<th>Method</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying</td>
<td>Air-drying at 50 °C for 10 min</td>
<td>Desiccator-drying under vacuum for 7 days</td>
</tr>
<tr>
<td>Drawing</td>
<td>Dry-drawing with rotating godets at 100 °C</td>
<td>Wet-drawing in 1:1 acetone/water bath and rotating godets</td>
</tr>
</tbody>
</table>

3. Results

3.1 Melt-spinning experiments

3.1.1 Melt-spinning of graphene-modified fibres

Multifilament yarns of graphene and polyamide 6 can be successfully spun for winding velocities up to 1,400 m/min. Inline draw ratios up to a factor of 2.0 are successfully applied. However, increased filament break can be observed for winding velocities above 1,400 m/min thus leading to instabilities of the melt-spinning process. Melt-spinning of graphene/PA6 yarn is stable at 1,400 m/min for over 30 minutes delivering enough amount of yarn for further processing.

3.1.2 Properties of melt-spun fibres

Analysis of melt-spun filament yarns is made via optical- and scanning electron microscopy. In figure 2, an optical microscopy image of the melt-spun multifilament yarns is presented.

![Graphene agglomeration and graphene particles in the polymer matrix](image)

Fig. 2: Light microscopy image of graphene/PA6 filament

As it can be seen in the optical microscopy image, the graphene layers at some areas tend to build up agglomerations leading to inhomogeneities in the fibre diameter. We suppose that agglomeration already occurs during the compounding process thus underlining the demand on research within the field of nano-material processing techniques already before the actual fibre spinning process. However, with increasing draw ratio, the homogeneity of the fibre surfaces increases which can be interpreted as shearing of agglomerations. A scanning electron microscopy image of a multifilament with applied draw ratio of 2.0 is presented in figure 3.
The electrical conductivity of the obtained multifilament yarns is investigated via two-point DC tests. Crocodile clamps are placed onto the fibre with a distance of 2, 4 and 6 cm and the Ohmic resistance is noticed from the measurement device. Ohmic resistance per length is subsequently determined via linear regression over the values taken at the named distances (R_Ω/l) and the specific resistance is finally determined by multiplication with the surface area of the multifilament yarn. As only the electric conductivity in fibre direction is from relevance, the electrical conductivity is determined via inversion of the specific resistance. In table 4, the obtained values in dependency on the applied fibre draw ratio are presented.

<table>
<thead>
<tr>
<th>Fibre draw ratio</th>
<th>Electrical conductivity σ [10^-6 S/m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>6.8 ± 0.50</td>
</tr>
<tr>
<td>1.3</td>
<td>10.8 ± 4.00</td>
</tr>
<tr>
<td>1.5</td>
<td>6.2 ± 0.1</td>
</tr>
<tr>
<td>1.7</td>
<td>1.7 ± 0.3</td>
</tr>
<tr>
<td>2.0</td>
<td>14.0 ± 2.00</td>
</tr>
</tbody>
</table>

In general, there is a tendency of decreasing conductivity values with increasing draw ratio. However, the last measurement value with a draw ratio of 2.0 has to be considered separately as the mass throughput of the spin package in the melt-spinning plant was increased during melt-spinning trials. The decrease of electrical conductivity can be explained with a defoliation of the graphene platelets inside the polymer matrix which sabotages the percolative network in the fibre matrix. Similar measurements for melt-spun- and drawn fibres with Carbon Nanotubes in polymeric fibres were made in previous experiments [11].

### 3.1.3 Weaving and processing to textile supercapacitor

The as-spun graphene multifilament yarns are processed to woven fabrics whereby the graphene/PA6 yarns are incorporated in warp- as well as in weft-direction into the woven fabric. Besides plain-weave woven fabrics, also atlas fabrics are prepared. 1.5 meter of plane-weave woven fabric and 2.5 meters of atlas fabrics are produced whereby a warp- and weft density of 25 cm⁻¹ is achieved. A photograph of the obtained woven fabrics is presented in figure 4.
As it can be deduced from figure 4, there are some disorders in the structure of the woven fabrics. This can be explained by several difficulties during weaving, as there are friction effects between the weft yarns. Furthermore, during weaving some filaments are knotting which leads to greater filament tensions and finally to a rupture. In comparison to neat polyamide yarns which are significantly easier in processing, this is caused by the fact that addition of graphene leads to a roughening of the fibre surface, which is for example clearly visible in the optical- and electron microscopy images (figures 2 and 3). Subsequently, the woven fabrics are processed to a textile supercapacitor as described in the chapter above. A schematic overview of the textile supercapacitor is presented in figure 5.

3.1.4 Capacity of textile supercapacitor

The textile supercapacitor is connected to a power source and load for one second at 1.25 Volt. After that, discharging curve is recorded by an oscilloscope. The corresponding discharge curve is presented in figure 6.
As it can be seen in the discharging curve, discharging occurs in almost one second. This can be explained by leakage currents and self-discharging as there is no separator layer between the graphene electrodes. Furthermore, there are small weaving defects in the woven fabric visible which enable leakage currents between the current collector and the electrolyte. However, quasi-reversible redox reaction occur during the charging and Helmholtz double layers build up which lead to the typical, exponential discharge behaviour of supercapacitors which can be also seen in the recorded curve.

From the discharging curve and the obtained resistance of the woven fabric, the capacity of the prepared textile supercapacitor can be determined. In Table 5, the obtained capacity for plain-weave- and atlas woven fabrics are presented with respect to the supercapacitor’s mass and surface.

<table>
<thead>
<tr>
<th>Bonding type of woven fabric</th>
<th>Capacity per mass $C_a$ [mF/g]</th>
<th>Capacity per area $C_a$ [$\mu$F/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atlas woven fabric</td>
<td>1.14 ± 0.06</td>
<td>37.88 ± 2.10</td>
</tr>
<tr>
<td>Plain-weave woven fabric</td>
<td>1.82 ± 0.24</td>
<td>57.31 ± 7.68</td>
</tr>
</tbody>
</table>

The obtained gravimetric capacity of the plain-weave woven fabric is about 60% higher than the capacity of the supercapacitor basing on an atlas woven fabric. Mainly responsible for this observation is the fact that the plain-weave woven fabric possesses a higher density thus offering a higher electrode area than the atlas woven fabric. However, in comparison to the graphene yarns presented in the introduction chapter, these values are three- up to five decimal powers lower. Nevertheless, the hereby prosecuted melt-spinning approach is important and well-promising as this technique offers the possibility of low-cost fabrication of graphene-modified yarns for textile applications. For instance, if a palm-size woven fabric with a warp- and weft-density of 25 insertions per cm shall be produced, at least about 35 meters of graphene-modified yarn are required. As it can be deduced from the state of the art of wet-spinning approaches, only a few meters can be produced with this technique which is not sufficient for industrial demands. By use of the hereby published melt-spinning approach, 35 meters of graphene-modified filaments can be fabricated in less than one second, rather than after several days. Furthermore, it is expected that graphene mass concentrations above one percent can be introduced in the polymer matrix in advanced spinning trials, which will lead to an increase of the electrical conductivity and thus to higher capacity values of textile supercapacitors containing melt-spun graphene/PA6 fibres.

3.2 Wet-spinning experiments

3.2.1 Structural properties of wet-spun fibres

In figure 7, a SEM-image of a PVA/graphene filament is presented.
As it can be derived from the microscopy images, the graphene flakes agglomerate in the fibre during spinning process leading to inhomogeneous fibre geometries. Mainly responsible for this observation are in-constant spinning conditions, i.e. varying winding velocities and varying mass throughputs during coagulation. In figure 8, the agglomerations are visible more detailed whereby the presented filaments were dried thermally with subsequent wet-and dry-drawing.

Due to the existence of graphene agglomerations, fissures of the fibre surface occur if the fibres are drawn in a subsequent step. Therefore, a SEM image of wet-drawn- and previously desiccator-dried filaments is presented in figure 9.
The increased appearance of graphene agglomerations can be explained by several reasons: On the one hand, the graphene layers naturally tend to agglomerate due to their enormous surface energy. In contrast to the already published works of graphene oxide fibres, there is no development of a nematic phase in the spinning solution due to missing covalent- and hydrogen-bonding interaction between graphene and the surrounding medium. Furthermore, there are process-based reasons for agglomerations as there is not a constant winding velocity in the wet-spinning process available.

3.2.2 Mechanical properties of wet-spun fibres

The mechanical properties of the graphene/PVA filaments are analysed via tensile tests. Each filament type is analyzed three times. The results of the measurements are presented in figure 10.

By addition of graphene into PVA polymer matrix, the tensile strength of the obtained filaments is increased about one magnitude and the elongation is reduced significantly. For neat PVA filaments, a tensile strength of 3.15 ± 0.36 MPa is measured whereby in the case of addition of 10 wt% of graphene, the tensile strength increases to 21.47 ± 3.07 MPa. Furthermore, after-treatment of the graphene-PVA fibres does almost lead to a doubling of the tensile strength in comparison to untreated PVA/graphene fibres (40.59 ± 7.82 MPa and 37.55 ± 2.10 MPa for wet- and dry-drawn yarns, respectively). The values obtained for drawn PVA/graphene filaments are comparable to tensile strength values obtained by other research groups which make graphene attractive as additional material for polymer matrices without further reduction.

4. Summary and outlook

In this work, the successful development of a textile supercapacitor by use of melt-spun graphene/PA6 filaments is presented. Furthermore, it was possible to perform melt-spinning experiments with graphene in polyamide 6 at 1,400 m/min which has not been reported so far. The obtained filaments show electrical conductivities in the order of 10^{-5} S/m which is seven orders of magnitude higher than the conductivity of unmodified polyamide 6. The capacity of the textile supercapacitors was determined in the mF/g regime which is on the one hand several magnitudes lower than the obtained, wet-spun graphene fibre supercapacitors [12-15]. On the other hand, the hereby presented approach opens the door towards an economically friendly path for textile supercapacitors as the production velocity of the as-spun graphene yarns is about three orders of magnitude higher than the wet-spun graphene yarns. Tasks for further development will be to increase the graphene amount in polyamide 6 and
furthermore the improvement of the supercapacitor development for reduction of leakage currents and self-discharging which will lead to significantly higher capacities.

In the frame of wet-spinning experiments, graphene is incorporated into PVA and the influence of graphene onto the structural and mechanical properties is investigated. For spinning of the monofilaments, a lab-scale piston spinning plant is used. Analysis via optical- and electron microscopy shows agglomerations of graphene in the fibre. However, the incorporation of graphene into PVA lets to an increase of the tensile strength about a factor of 10 underlining the potential of graphene for high-performance, fibre-based composite materials. With additional steps like drying and drawing, a further increase of the tensile strength is achieved. As future work, a pilot-scale- and continuous wet-spinning process at technical scale including the named post-treatment steps has to be developed in order to obtain high-throughput production of fibres with high stiffness.

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