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Polymeric Sensor Fibers Based on a Piezoelectric Polymer and Metal Alloy/Carbon Nanotube/Polymer Composite for Structural Health Monitoring

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Sensor fibers can be used for structural health monitoring in multiple environmental applications. Possible areas of applications are in geotextiles for monitoring the status of the reinforcement or in wind energy plants to monitor the load on wind blades. In this paper, a new type of sensor fiber based on a piezoelectric polymer (polyvinylidene fluoride) and a composite material made of a thermoplastic polymer, a low melting point metal alloy and carbon nanotubes (CNT) is presented. The piezoelectric polymer generates a signal when a load is applied if it is processed in the right way. Here, the formation of the piezoelectric crystalline structures will be presented. The conductive compound transmits the signal to measurement equipment. While CNT form a conductive network in the polymer, the metal alloy acts as a coating for the nanotubes and increases the electrical conductivity (100 S/m) by two orders of magnitude compared to pure CNT nanocomposites (approx. 1 S/m). The increased conductivity allows the transmission of the signals over larger distances, making the material favourable for large scale applications like wind blades.

1. Introduction

Piezoelectric sensor fibers allow the transformation of mechanical stress on the fiber into an electric signal by making use of the direct piezoelectric effect. Beside ceramic fibers (e. g. PZT-based), the piezoelectric polymer poly(vinylidene fluoride) (PVDF) can be applied. One of the most promising applications is the structural health monitoring (SHM) in fiber reinforced plastics. If the fibers are directly placed into the matrix material (beside the reinforcing fibers), an external contacting is necessary for measuring the electrical signal generated in the fibers, which becomes impossible if carbon fibers are applied as a reinforcing material (Walter et. al., 2012). For this case, the use of bicomponent sensor fibers, which allows the contacting of single fibers, is much more useful. Furthermore, mechanical stresses can be measured with a certain spatial resolution by placing the fibers into a grid (Glauß et. al., 2013).

1.1 Piezoelectric polymeric fibers

The piezoelectric effect in the polymer poly(vinylidene fluoride) is based on the formation of a special crystalline phase, where the polar polymer chains are ordered regularly in an all-trans conformation. This so called β phase can be obtained by applying mechanical stress (in chain direction) or an electrical field (perpendicular to polymer chains). In the fiber spinning process, β phase is mainly formed during solid state drawing (Steinmann et. al., 2011). Since β phase crystals are ordered only in one direction (fiber axis) and randomly placed in the fiber cross-section, they need to be aligned by a poling process in an electrical field with E > 35 kV/mm. For bicomponent fibers, the poling can be achieved by using the conductive core material as one electrode and an external coating as the second one (Glauß et. al., 2013).

1.2 Conductive polymer nanocomposite fibers

One of the most relevant processes for making electrically conductive fibers is the modification of a non-conductive polymeric matrix with electrically conductive fillers. For most of the applications, fiber diameters far below 100 µm are desirable, which makes it necessary to use nano-scaled fillers, like carbon nanotubes

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(CNT) or special carbon blacks (CB) with a reduced particle size. After the modification, which is usually performed in a solution mixing or melt mixing process (compounding) (Ma et. al., 2010), the polymers can be spun out in the corresponding melt (Deng et. al., 2011) or solution spinning process (Chae et. al., 2005). In the recent years, many material combinations have been examined.
One of the most important parameters is a homogeneous distribution of the fillers in the polymeric matrix, since aggregates lead to fiber breakages in the spinning process and an irregular diameter over the fiber length. For particles like CNT, the percolation threshold (where the fillers form a conductive network in the polymeric matrix) in fibers can be usually found between 2 and 7 w% (filler concentration) (Moore et. al., 2004). The plastic deformation in the molten or solved state of the polymer and also solid state drawing have a huge influence on the electrical conductivity, since 1D or 2D shaped particles can be aligned in the processes (Bhattacharyya et. al., 2003). After solid state drawing, the conductivity usually achieved in the fibers is between 10^{-3} and 10^{-1} S/m. Only by applying a subsequent heat treatment close to the melting temperature of the polymer, the original conductive network can be restored and values of up to 100 S/m can be achieved (Deng et. al., 2011). This process is not suitable if the fibers have to remain soft because of the shrinkage occurring at elevated temperatures.
Compared to bulk materials, which can be usually mechanically improved by using nano-scaled fillers, the conductive additives act as an impurity in the case of fibers. This leads generally to increased stiffness, lower strength and a lower maximum elongation (Kumar et. al., 2002).

1.3 Aim of this study

As mentioned before, one of the most promising options for piezoelectric sensor fibers is the application in structural health monitoring of composite materials. Especially for larger parts where failure would become extremely critical (e. g. wind blades or structural parts of aircrafts), the current combination of the conductive compound and the piezoelectrical polymer is not sufficient for transferring the electrical signal over the necessary distances (1 m and above).
As the piezoelectric effect in PVDF is close to the maximum theoretic level, the more useful approach is the modification of the conductive compound. From injection moulding it known according to Michaeli et. al. (2010), that the electrical conductivity of a polymer/carbon nanotube composite material can be increased drastically by adding a low melting point metal alloy to the polymer. For fiber based materials, this approach has never been studied before. In this work, a polymer/carbon nanotube/metal alloy composite material is developed for increasing the electrical conductivity in the piezoelectric bicomponent sensor fibers. Beside increasing the electrical conductivity, the processability shall be improved by processing a molten metal phase which should lower the viscosity of the compound. Furthermore, it is demonstrated that the new conductive material has no negative influence on the formation of the piezoelectric β phase. The concept for the new fiber is shown in Figure 1.

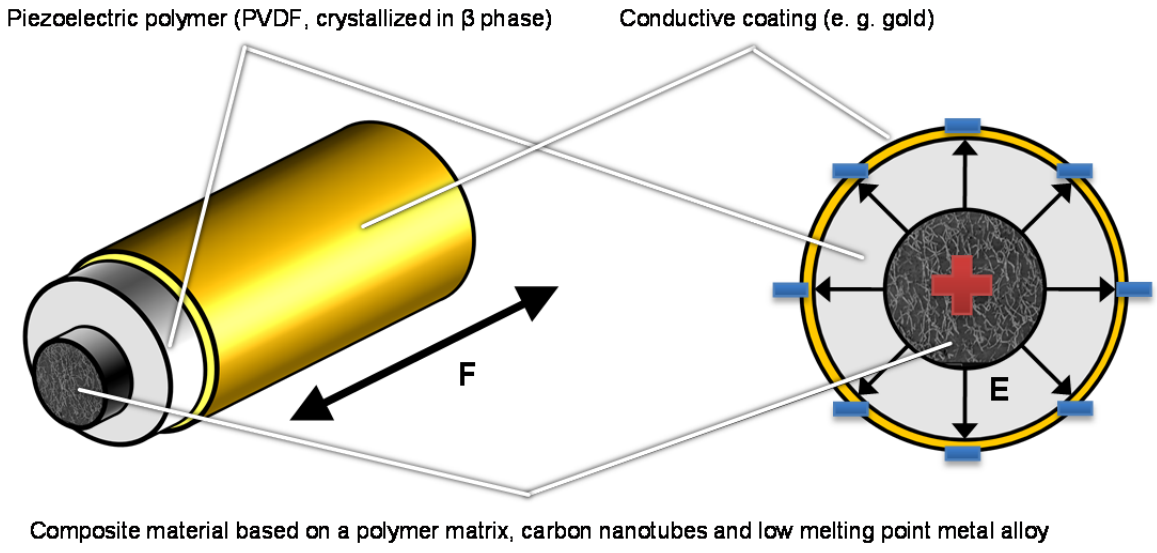

Figure 1: Concept for piezoelectric sensor fibers

Table 1: Material variations in the compounding process

Material number	Amount of PP [w%]	Amount of CNT [w%]	Amount of metal [w%]
1	87	3	10
2	85	5	10
3	80	10	10
4	77	3	20
5	75	5	20
6	70	10	20
7	67	3	30
8	65	5	30
9	60	10	30

2. Material selection

For the piezoelectric sheath, a suitable PVDF grade for fiber extrusion (SOLEF 1008 from Solvay Solexis s.a., Brussels, Belgium) is used. The material has a melting point of 177 °C. For the co-extrusion of the conductive core material, a base polymer with a compatible melting point has to be chosen. When comparing the melting points of the standard spinning polymers, polypropylene fits best to this requirement. Here, a fiber spinning grade (Moplen HP561R from LyondellBasell, Rotterdam, The Netherlands) is used. The material is modified with Carbon Nanotubes (CNT) from Nanocyl s.a., Sembreville, Belgium and a low melting point metal alloy (MCP 220 with a melting point of 220 °C) from MCP Hek GmbH, Lübeck, Germany.

3. Conductive polymer/CNT/metal allow composite

3.1 Compounding process

The base polymer is modified by compounding with a twin screw extruder from Brabender GmbH, Duisburg, Germany, whereas two gravimetric metering systems are used. Polypropylene and Carbon Nanotubes are filled into the first zone of the extruder. In the second zone, the metal pellets are added to prevent the separation of the materials in the beginning of the process. Different concentrations of CNT and metal alloy are chosen (see Table 1).

3.2 Electrical properties of the compounds

For analyzing the percolation behaviour of the compounds, the electrical conductivity is measured after the extrusion of the compounds. The result is shown in Figure 2. The value for electrical conductivity mainly depends on the CNT concentration in the composite material. By increasing the metal concentration, electrical conductivity an only be slightly improved and doesn't change if more than 20 w% of metal is compounded into the material. For further processing, the materials with 5 and 10 w% of CNT and a metal concentration of 20 w% are chosen.

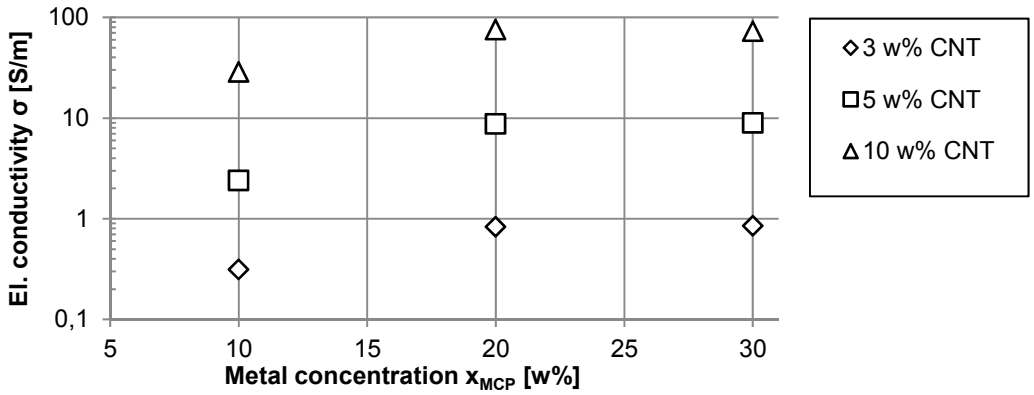

Figure 2: Electrical properties of the compounds (PP/CNT/MCP220)

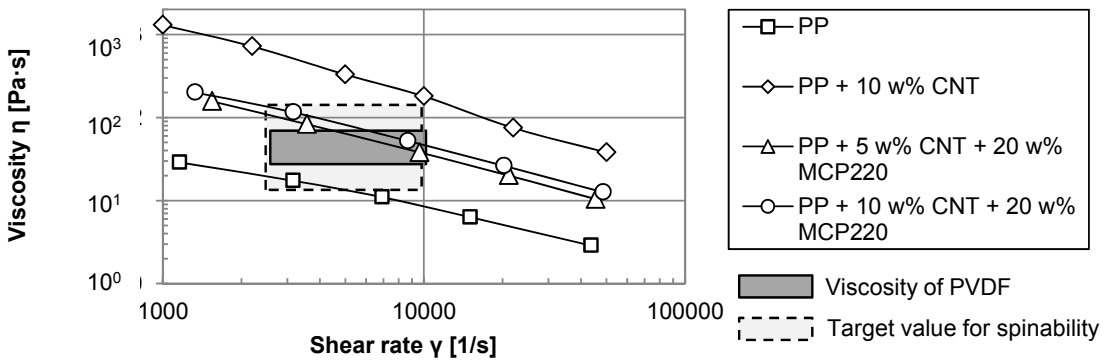

Figure 3: Rheological properties of the compounds (PP/CNT/MCP220)

3.3 Rheological properties of the compounds

The influence of the metal alloy on the rheological properties are measured with the help of a capillary rheometer (GÖTTFERT Werkstoff-Prüfmaschinen GmbH, Buchen, Germany). Shear rates are varied in the range 1.000 and 100.000 s^{-1}, which is the typical region for the melt spinning process. The results are shown in Figure 3. Compared to nanocomposites without any metal content, the viscosity can be drastically lowered. It is still higher than for pure polypropylene, but in the same region as the PVDF grade used for the trials. Therefore, the combination of the two materials seems to be very promising.

4. Melt spinning and drawing of core/sheath fibers

4.1 Spinning and drawing process

The two materials are combined in a co-extrusion process (bicomponent spinning) to core-sheath geometry. The machine used for the trials is a pilot scale spinning plant from Fourné Polymertechnik GmbH, Alfter, Germany. The parameters for the spinning process can be found in Table 2.
The solid state drawing process is performed at three different drawing temperatures (T_D = 80 °C, 120 °C and 160 °C). For each temperature, the maximum draw ratio is determined. The fibers are then drawn at one third, two third and the full draw ratio. For the three different temperatures, the following limits for the draw ratio (DR) can be found: DR = 5.2 (T_D = 80°C), DR = 5.8 (T_D = 120 °C) and DR = 7.1 (T_D = 160 °C).

4.2 Mechanical properties

The mechanical properties (tenacity and maximum elongation) are determined as a function of raw ratio and drawing temperature. The results are shown in Figure 4. The tenacity of the fibers constantly increases with increasing draw ratio, an influence of the drawing temperature is more or less not present. The maximum elongation first increases with increasing draw ratio, since the structures in the core can be oriented, which makes the fiber less brittle. This effect is much larger for high drawing temperatures, which make the alignment more easier. With increasing draw ratios, maximum elongation drops again, which is the result of more or less complete orientation of the polymer chains.

Table 1: Process parameters for melt spinning

Parameter	Value	
	Core (PP/CNT/metal)	Sheath (PVDF)
Pressure extruder	80 bar	60 bar
Extruder temperature (zone 1/zone 2/zone 3)	220 °C/225 °C/ 235 °C	210 °C/220 °C/ 230 °C
Temperature melt lines	240 °C	240 °C
Temperature gear pumps	250 °C	
Temperature spin pack	250 °C	
Throughput	3 cm³/min	6 cm³/min
Diameter spin hole	200 µm	350 µm
Melt draw ratio	11	41
Take-up velocity	250 m/min	

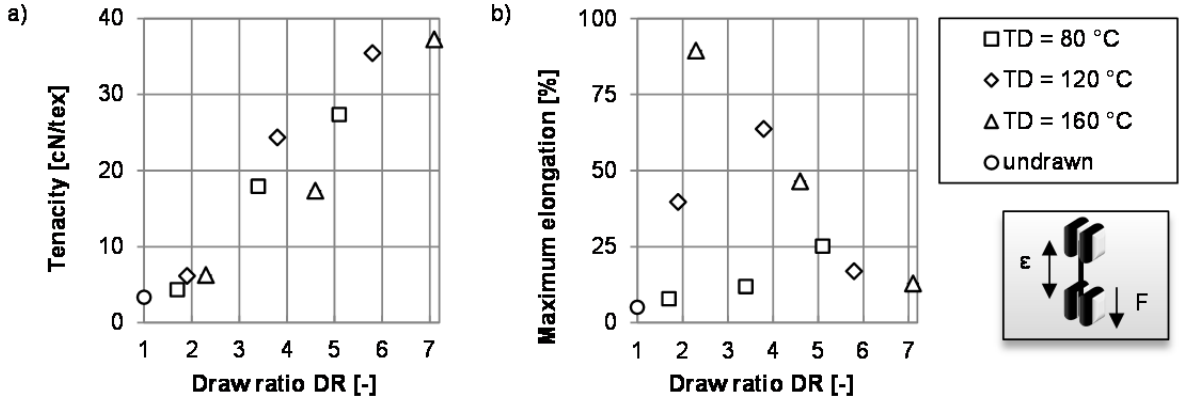

Figure 4: Mechanical properties of the fibers drawn at different temperatures, a) Tenacity as a function of draw ratio, b) Maximum elongation as a function of draw ratio#

4.3 Electrical properties

Electrical conductivity is analyzed as a function of draw ratio and drawing temperature. The results are shown in Figure 5 a). The drawing temperature has no influence on the electrical properties. For moderate draw ratios, electrical conductivity only slightly decreases, which is a consequence of increasing CNT orientation in the fibers.

For high draw ratios, a drop in electrical conductivity can be observed. Here, conductive networks of CNT are partially destroyed. Compared to nanocomposite fibers without any metal, electrical conductivity can still me measured, which seems to be an effect of the metal still making a conductive path between separated CNT.

4.4 Formation of piezoelectric crystal phase

The fraction of the piezoelectric crystalline phase is determined by wide-angle X-ray diffraction (WAXD). The calculation of the β phase fraction is performed according to Steinmann et. al. (2011). The results are shown in Figure 5 b). β phase fraction increases with increasing draw ratio, whereas lower draw ratios are needed at lower drawing temperatures because of the increased mechanical stress.

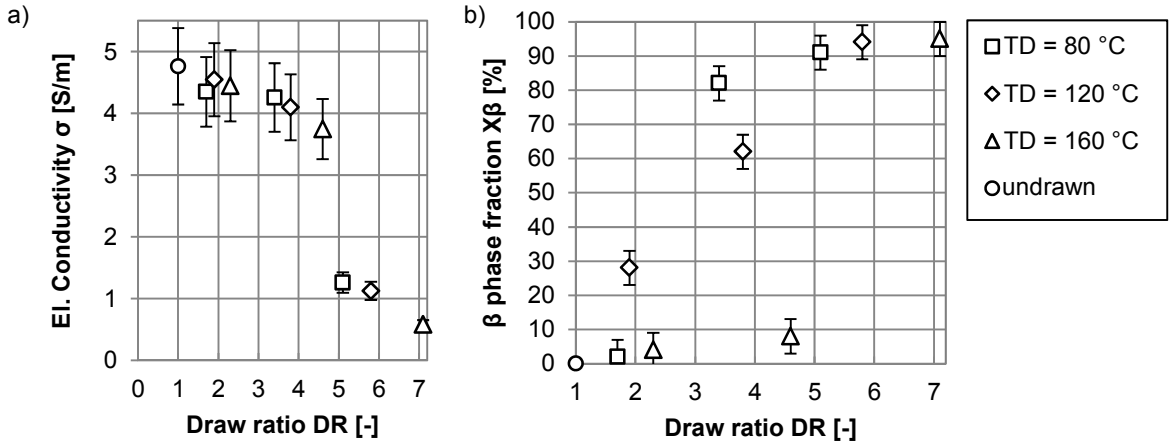

Figure 5: a) Electrical properties of the fibers drawn at different temperatures as a function of draw ratio, b) fraction of the piezoelectric crystalline phase (β phase) for fibers drawn at different temperatures as a function of draw ratio

5. Conclusion

It was demonstrated that the new conductive polymer compound based on polypropylene, carbon nanotubes and a low melting point metal alloy is very promising as a base material for piezoelectric sensor fibers. The electrical conductivity of the compound can be increased to nearly 100 S/m for 10 w% of CNT and 20 w% of metal and 10 S/m for 5 w% of CNT and 20 w% of metal. After spinning and drawing, the conductivity is still remaining, which can be attributed to the metal component stabilizing the conductive CNT network.
Furthermore, processability is enhanced by adding the metal component. The viscosity decreases to a suitable value for co-extrusion with PVDF and the melt spinning process is stable for up to 2 hours without filament breakage.
Suitable mechanical properties for textile and composite processing of the fibers can be obtained by using medium or high draw ratios. Furthermore, also the piezoelectric β phase is formed under this conditions.
In combination with the electrical analysis, fibers with medium draw ratios are the most promising candidates for structural health monitoring since all necessary properties can be achieved. For these fibers, a signal strength of more than 20 mV can be expected if a single filament is placed into a composite part with a size of 1 m. If the fibers are coupled to suitable electronics, this signal level is more than sufficient for a quantitative analysis of stress and strain in composite materials.
In the future, the polarization behaviour of the fibers has to be checked. A promising option would be the polarization during drawing. Furthermore, suitable concepts for sensor networks in composite materials have to be developed which allow the locally resolved measurement of stress and strain. Here, the fiber direction has to be considered, which offers the chance to resolve the direction of strain in the anisotropic materials.

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