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In the final step, a textile based on those fibres was prepared and its sensing behaviour was investigated on ethyl acetate and acetone clearly showing that such textiles are suitable to detect these solvents.

Multifilament fibres of poly(ε-caprolactone) / poly(lactic acid) blends with multiwalled carbon nanotubes as sensor materials for ethyl acetate and acetone

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Abstract

Conductive poly(ε-caprolactone) (PCL) + 4% multiwalled carbon nanotubes (MWCNTs) / poly(lactic acid) (PLA) = 50/50 wt% blend multifilament fibres were melt-spun and a woven textile was made by a handloom with the conductive fibres in weft direction. The fibres were tested for cyclic liquid sensing in ethyl acetate and acetone as two moderate solvents and in ethanol as a poor solvent. The liquid sensing responses, namely the relative resistance changes R_{rel} relating the resistance change to the initial resistance of the samples on contact with ethyl acetate and acetone were fast (R_{rel} higher than 16 after 100 s), with high amplitudes (R_{rel} higher than 32 after 500s), and well reproducible. At the same time, the fibres were resistant against these solvents. The response to ethanol was also reproducible, however, very slow and with low amplitude.

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1. Introduction

Carbon nanotube (CNT) filled polymer nanocomposites have been extensively explored in the recent years [1-16]. It is well known, that CNTs, used as filler in conventional polymers, can improve remarkably their mechanical and thermal properties. Moreover, when the concentration of CNTs exceeds a certain value (at which an electrical percolation occurs), the electrical conductivity of the polymer composite increases over several orders of magnitude. These conductive, flexible and easy processable thermoplastic materials can find a lot of applications in electronics and medical physics as smart materials. In particular, when a CNT / polymer composite responds to certain external stimuli with an electrical resistance change, it may be used as a sensor [17, 18]. Several phenomena are discussed to contribute to the resistance changes for gas, vapour, or liquid sensors [see 19, 20]. In summary, the resistance changes seem to be due to a combination of a spatial deformation of the CNT network due to the swelling of the polymer matrix and the interactions between nanotubes and solvent/gas/vapour molecules [19-21]. Both lead to an increase in the nanotube-nanotube

distance of neighboring tubes which reduces the tunneling current. A number of reports on sensing of vapours [22-29], gases [30-41], mechanical stress [42-44], temperature [45] and pH [46] by means of CNT / polymer based films or fibres have been published.

Up to date, only a few studies on liquid sensing properties of CNT / polymer composites have been reported on compression-moulded plates [19, 21, 47] and melt-spun monofilament fibres [48]. In addition, some recent reports concern liquid sensing measurements on polymer blend based plates and melt drawn filaments containing CNTs in one phase [49]. For immiscible polymer blends containing carbon black [50-54] or polyaniline [54, 55], intense investigations on liquid sensing filaments produced using a capillary rheometer have been reported in the literature.

Melt-spun fibres can be easily woven in textiles and large area sensors can be produced. These textile sensors should be able to detect leakages in tanks and containers for industrial solvent storage. It is not an easy task to choose suitable nanocomposites for producing fibres for woven textile sensors. The nanocomposites should be melt-spinnable and sensitive to at least one liquid, but at the same time durable. It would be also advantageous if such large dimension sensors can be recycled or degraded after finishing their lifetime [56]. Melt-spinnability of polymer / CNT nanocomposites is assumed to be better than of composites with CB: However, melt-spinning is not trivial, as the melt viscosity of the composite increases with increasing CNT volume fraction. Blending the CNT / polymer composite with a second polymer phase is a way to tune the viscosity of the composite and to combine favourable properties of both blend phases. However, the both phases should be resistant against the tested solvents. In order to achieve strong and reproducible liquid sensing responses, the polymer composite / solvent system should be properly chosen. Materials with high solubility in a certain solvent can work successfully as vapour sensors, but will be dissolved in the liquid phase. On the other hand, the electrical response on weak solvents will

be not sufficient. Thus, a moderate solvent should be chosen, which only swells both polymers, without destructing them.

On the other hand, blends should be favourable compared to single composites as nanotubes make (in most cases) a matrix more brittle, which can be compensated by adding a second continuous component. When using polymer blends with both phases swelling in a similar manner, this provides a better durability during sensing as compared to blend phases swelling in different manner.

In this contribution, we have investigated the liquid sensing properties of melt-spun multifilament fibres from a blend of poly(ε-caprolactone) (PCL) containing 4 wt% multiwalled carbon nanotubes (MWCNT) and poly(lactic acid) (PLA). PLA is a well spinnable bio-based thermoplastic, which has gained recently a lot of interest in the textile industry [57, 58]. Both, PLA and PCL are biodegradable and can be decomposed under special conditions on environment friendly low molecular substances and the CNTs may be recycled. The widely used solvents acetone and ethyl acetate were chosen as moderate solvents for both, PLA [59, 60] and PCL [61, 62]. Reference measurements were done with ethanol representing a weak solvent. The polymer structure was investigated before, during and after immersing of the fibre in the solvents.

2. Materials, fibres and textile preparation

PCL CAPA® 6400 (SOLVAY), PLA Nature Works 6201 (Cargill, representing a granular mixture of 98.7 wt % PLLA and 1.3 wt % PDLA) and MWCNT Nanocyl™NC7000 (Nanocyl S. A., Belgium) were used in this study.

The multifilament fibres were produced in two main processing steps. The first one consisted in incorporating 4 wt% MWCNT into the PCL using a Thermo-Haake co-rotating intermeshing twin-screw extruder with a screw diameter of 16 mm and a length to diameter ratio of 25. This extruder includes five heating zones in which the temperature was

independently and gradually fixed from 55 to 80 °C (details in Table 1). The screw rotational speed was fixed at 100 rpm. PCL and MWCNT were manually introduced in the feed hopper. The obtained strand (rod with 1.5 mm diameter) was pelletised for the following spinning step. In order to remove the absorbed water, before extrusion or spinning the pellets were dried for 12 hours at 80 °C (PLA) and 50 °C (PCL).

In the second step, the PCL + 4 wt% MWCNT composite material was premixed with equal weight amounts of pure PLA resulting in PCL + 4% MWCNT / PLA = 50/50 wt% blend. The melt flow index (MFI) for PCL + 4 wt% MWCNT at 215°C and a load of 2.16 kg was measured to be 3.5 g/10 min, whereas pure PLA had a MFI of 28.5 g/10 min. Both granules were fed directly in the hopper of the melt spinning machine (driver SPINBOY I manufactured by Busschaert Engineering, Belgium) which is schematically represented in Figure 1. After passing through the single-screw extruder of this spinning machine, the molten polymer blend containing nanotubes is forced through a die head with a rather low diameter (1.2 mm), and through a series of filters. Two bundles of monofilaments were obtained which are cooled in air and combined into a multifilament. This melt-spun multifilament contained 80 monofilaments (2 dies x 40 holes), was covered with a spin finish oil, and rolled up on two heated rolls with varying speeds (S1 and S2) to ensure a draw. The theoretical drawing of multifilament is given by the draw ratio DR = S2/S1. In this study, a low DR was applied (S1 = 80 m/min, S2 = 90 m/min and DR = 1.12) which entailed that the obtained multifilament has a large diameter; the count of the multifilament is around 1270 tex (which corresponds to an average diameter of the monofilament equal to 143 μm). Table 1 summarizes the parameters used in the two steps of the multifilament preparation.

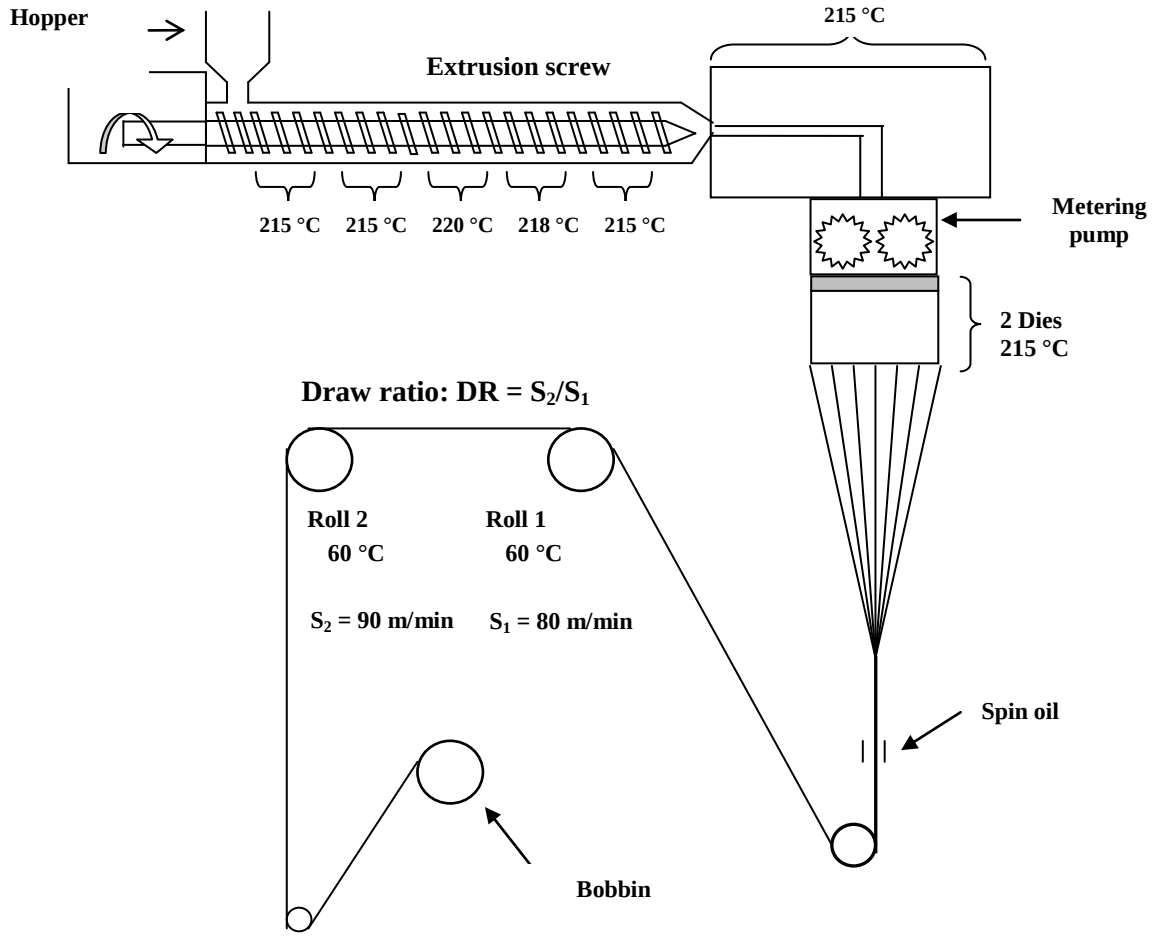


Figure 1: Schema of the spinning technology of PCL + 4% MWCNT / PLA = 50/50 wt% blend.

Table 1: Conditions of preparation of PCL + 4% MWCNT composite (step 1) and PCL + 4% MWCNT / PLA = 50/50 wt% blend (step 2).

Step 1 : PCL + 4wt.% MWCNT					
Screw speed (rpm)	**Temperature (°C)**				
N	T_1	T_2	T_3	T_4	T_5
100	55	65	70	75	80
Step 2 : PCL + 4% MWCNT / PLA = 50/50 wt%					

Temperature (°C)							**Roll 1**		**Roll 2**	
T_1	T_2	T_3	T_4	T_5	T_6	T_7	Tr_1 (°C)	S_1 (m/min)	Tr_2 (°C)	S_2 (m/min)
215	215	220	218	215	215	215	60	80	60	90

In order to increase the cohesion between the monofilaments in the fibre, a twist was applied to the multifilaments resulting in a yarn twist of 28 tr/m in Z direction.

Concerning the textile production, as weaving device the sample weaving loom Patronic B60 from ARM was used. It allows making fabrics with a width which can go up to 50 cm and consists of the following elements: 24 frames equipped with heddles (24 cm) allowing selecting warp yarns, 2 beams of warp yarns, 2 pedals or one crank with hand. The pedals movements and the automaton (Selectron) allow raising and lowering the frames. The upper and lower layer of warp yarns which is called shed is obtained. This allows the weaver to insert the weft yarn. The insertion of the weft yarn (perpendicularly at warp yarns) is manually made thanks to a shuttle conveying a small bobbin.

In our study, warp yarns are twisted acrylic yarns (orange), and weft yarns are the conductive PCL + 4% MWCNT / PLA = 50/50 wt% multifilaments (black). The weave pattern realized is a satin weave 4 with density of warp yarns of 16 yarns/cm and weft yarns of 5 yarns/cm and a total width of 30 cm.

In Figure 2, two kinds of woven textile parts are remarkable. The orange/black parts correspond to the conductive textile strip describe above. The grey/blue parts allow to separate conductive parts with insulating woven fabric thanks to insertion of cotton yarn in weft direction instead of the conductive PCL + 4% MWCNT / PLA = 50/50 wt% multifilament.

3. Experimental methods

3.1 SEC measurements

The SEC (size exclusion chromatography) measurements on PCL + 4% MWCNT / PLA = 50/50 wt% fibres (as-spun and after 6 h treatment with ethyl acetate and acetone and subsequent drying) were done on liquid chromatograph Agilent 1100 Series (Aglient, USA)

equipped with refractive index (RI) detector and PL Gel MIXED-B-LS separation column (Polymer Laboratories, UK). The calibration was done using a polystyrene standard. Chloroform with a flow rate of 1 ml/min was used as eluent. In order to remove the MWCNTs, the samples were dissolved in chloroform at room temperature (at least over night) and the dispersions were filtered with a PTFE filter with a pore size of 0.2 μm. The concentration of the eluent solution was 4 mg polymer/ml eluent.

3.2. Mechanical measurements

The tensile tests were performed on untreated and solvent treated PCL + 4% MWCNT / PLA = 50/50 wt% fibres using a material testing machine Z010 (Zwick GmbH & Co. KG). The solvent treated fibres were kept in acetone and ethyl acetate for 6 h at ambient temperature and subsequently dried at air for one week. The multifilament fibres were glued together at the end and clamped in the measuring cell. The investigated length and the drawing velocity were 30 mm and 10 mm/min, respectively. 4 pieces of the untreated fibres, 5 pieces of acetone treated, and 5 pieces of ethyl acetate treated fibres were measured and mean values and standard deviation are given. The measurements were done under standard conditions of 50 % relative humidity and 23 °C.

3.3. Scanning Electron Microscopy (SEM)

The morphology of the PCL + 4% MWCNT / PLA = 50/50 wt% blend was studied using a scanning electron microscope Ultra 55 plus (Carl Zeiss SMT). The multifilaments which were embedded in epoxy resin were cut under liquid nitrogen and covered with a 5 nm sputtered platinum layer. In order to study the localization of the MWCNTs in the blend, the PCL phase was etched out with acetic acid at ambient temperature. The solvent was changed tree times in several hours' intervals. The weight of the etched sample was 51 % of the initial one, which indicates that the PCL phase was successfully removed. On the other hand, during the etching

the solvent remained transparent, indicating that the most of the MWCNTs remained in the sample.

3.4 Wide Angle X-Ray Diffraction (WAXD)

The WAXD measurements were performed using a P4 Diffractometer (Bruker AXS Karlsruhe) in transmission mode. Cu-K_α radiation was selected by primary graphite monochromator. The scattering curves were collected for 600 s (dry and swollen samples) and 60 s (swelling samples) using a two-dimensional HiStar / GADDS detector. The radial intensity distribution I(2Θ) (with steps $\Delta 2\Theta = 0.1°$) in a scattering range $2\Theta = 2$ to 41° was determined by sectoral integration in an azimuthal interval $\Delta\varphi = \pm 45°$. The fibre orientation was negligible, because of the low draw ratio.

The fibre was inserted in a glass capillary with 1.8 mm inner diameter. In order to have enough space to swell, the number of the monofilaments was reduced to the half. The different swelling stages were recorded repeatedly after filling the capillary with solvent. In order to replicate the crystallization conditions during the liquid sensing test, the sample was dried not in the capillary, but in ambient conditions after 6 h swelling in ethyl acetate / acetone and then put in the capillary for diffraction measurements.

3.5 Liquid sensing

The liquid sensing behaviour of the multifilament fibres was monitored by recording the resistance change during several immersion / drying cycles. The fibres were fixed between two crocodile clamps with a distance of 7 mm. Plastic conductive carbon cement (Leit-C-Plast – Neubauer Chemikalien) shown to be not sensitive to the used solvents was applied to the contacts in order to reduce the contact resistance. The wetting of the electrodes did not influence the results, because the resistance of the solvents was one order of magnitude higher than that of the unswollen and swollen sample. The resistance was measured by means of a

Keithley digital multimeter 2001 (measuring range 10^{-6} – 10^{9} Ω) connected to a personal computer.

The initial resistance of the fibre was recorded for 100 s with a sampling period of 1 s and then the sample was immersed in the solvent and the resistance was recorded with sampling periods of 1 or 2 seconds. Subsequently, 10 immersion (500 s) / drying (1000 s) cycles were periodically repeated for ethyl acetate and acetone, whereas for ethanol 3 cycles of 500 s immersion and 2000 s of drying were used. The relative resistance change R_{rel} was calculated following Equation 1, where R and R_i are the actual resistance and the initial resistance, respectively.

$$R_{rel} = \frac{R - R_i}{R_i} \qquad \text{Equation 1}$$

In order to compare the results from the first and second measurement of the same sample in ethyl acetate, the relative resistance change R_{rel} for the second measurement was calculated using R_i of the as-spun state.

The liquid sensing of the textiles was measured on textile parts (90 x 80 mm) cut from the produced textile using two brass electrodes with 50 mm distance. These were covered on their contact side with Plastic conductive carbon cement and connected to the Keithley digital multimeter 2001 (Figure 2). The assembly was placed on an isolating Teflon substrate. At the beginning of every cycle the sample was wetted with 2 ml solvent using a syringe by drawing a solvent line in the middle of the two electrodes (see arrow in Fig. 2). After about 10-15 s the whole sample was completely wetted and the resistance was recorded during the wetting and drying processes. The measurements started immediately after the first contact of the solvent. After 5300 s the textile was wetted again and 5 cycles were performed.

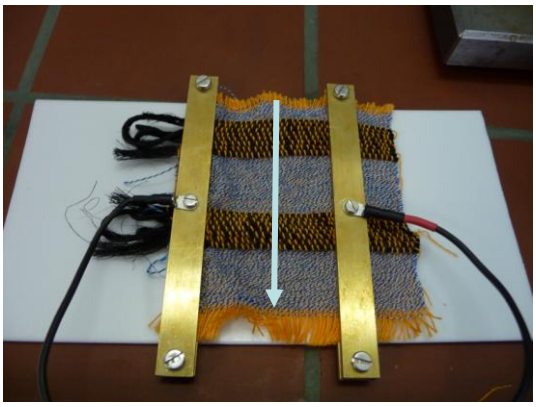


Figure 2. Textile sample fixed between two brass electrodes and placed on a Teflon substrate with the solvent line drawn initially.

4. Results and discussion

4.1. Size exclusion chromatography (SEC)

SEC measurements were performed in order to see the effect of solvent treatment on the molecular weight of the polymer chains in the fibres, i.e. whether some sample degradation occurred or not. The SEC data are presented in Table 2. The results reveal that the immersion of the PCL + 4% MWCNT / PLA = 50/50 wt% multifilament fibre in acetone and ethyl acetate does not lead to remarkable sample degradation. The increase in molecular weight after solvent treatment can be explained by dissolving of low molecular fractions of the blend which seems to be similar in both solvents.

Table 2. Molecular weights M_n and M_W and the polydispersity index M_w/M_n of PCL + 4% MWCNT / PLA = 50/50 wt% fibres (as-spun and after 6 h treatment with ethyl acetate and acetone) measured by SEC.

	M_n (g/mol)	***M_w (g/mol)***	***M_w/M_n***
PCL + 4% MWCNT / PLA = 50/50 wt%	18800	102900	5.49

PCL + 4% MWCNT / PLA = 50/50 wt% ethyl acetate	33400	104800	3.14
PCL + 4% MWCNT / PLA = 50/50 wt% acetone	34900	103500	3.00

4.2 Mechanical measurements

The influence of the solvent on the mechanical properties of the PCL + 4% MWCNT / PLA = 50/50 wt% fibres was proved by tensile tests. Table 3 shows several mechanical parameters of the as-spun and solvent treated multifilament fibres derived from the stress-strain curves: F_M, the maximum force; $R_{M,}$ the stress at this force related to the fineness of the filaments; $\sigma_{M,}$ the stress at this force related to the cross-section; and $\varepsilon_{M,}$ the elongation at the maximum force. Above reaching the maximum force F_M single fibres start to break leading to stepwise decreasing stress values with further elongation in the stress-strain diagrams of the multifilaments. The elongation ε_M is similar within the error interval for as-spun and solvent treated fibres, which also holds for F_M, R_M and σ_M values for the as-spun and ethyl acetate treated samples. However, F_M, R_M and σ_M decreased by about 50 % for the sample treated with acetone.

Table 3. Results of tensile tests on PCL+4 wt% MWCNT / PLA = 50/50 wt% multifilament fibres, as-spun and after 6 h treatment with ethyl acetate and acetone.

	as-spun sample	dried sample after 6 h treatment in ethyl acetate	dried sample after 6 h treatment in acetone
F_M (cN)	2856 ± 153	2779 ± 402	1561 ± 467
R_M (cN / tex)	2.1 ± 0.1	2.1 ± 0.3	1.2 ± 0.3
σ_M (MPa)	22 ± 1	22 ± 3	12 ± 4
ε_M (%)	6.2 ± 0.8	8.9 ± 1.2	6.6 ± 2.0

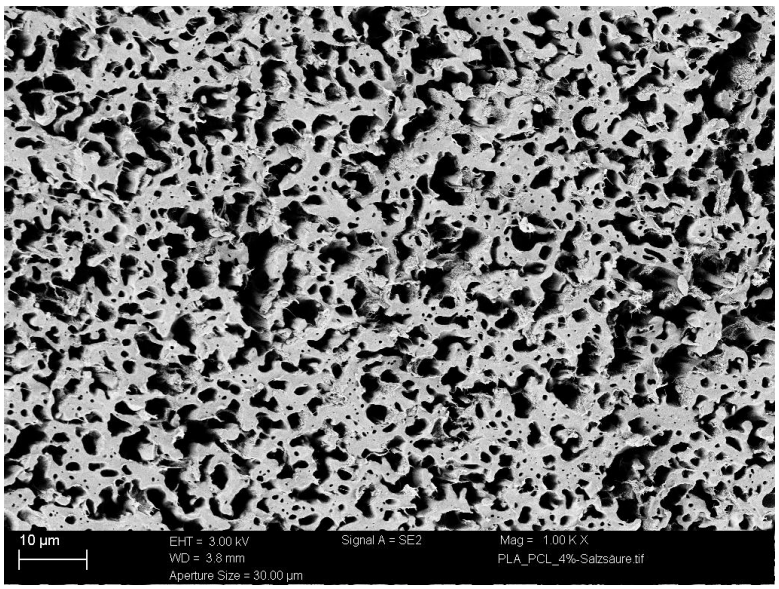
4.3. Morphology of the blend fibres using SEM

SEM was performed in order to study the blend morphology, the nanotubes dispersion, and the localization of the MWCNTs in the polymer blend. Figure 3 a) reveals the blend morphology of the PCL + 4% MWCNT / PLA = 50/50 wt% fibres on extracted samples, in which the remaining PLA phase is seen in grey. The dark areas represent the holes remaining after dissolving the PCL phase with acetic acid. The blend shows a co-continuous morphology. In order to understand better the liquid sensing mechanism in the PCL+4 wt% MWCNT / PLA = 50/50 wt% blend system, it is interesting to determine the localization of the MWCNT. As it was described before, the MWCNTs were first incorporated into the PCL phase.

However, in principle also a change of localization from a premixed phase into the other phase is possible, as a study on polycarbonate/poly(styrene-acrylonitrile)/MWCNT composites has shown recently. In that case, independently from the mixing sequence and even after premixing in poly(styrene-acrylonitrile), the MWCNTs migrated into the polycarbonate phase [63]. Investigating PCL/PLA/MWCNTs composite blends, similar to the blend system presented here, Wu et al. have found that the MWCNTs are localized in the PCL phase [64]. Two studies of PCL+MWCNT / PP blends [49, 65] have revealed that the MWCNTs remain in the PCL phase. However, by mixing of PCL+6% MWCNT with PA12, the MWCNTs migrated in the PA12 phase [65].

SEM images of the PCL + 4% MWCNT / PLA = 50/50 wt% fibre with two different magnifications as presented in Figure 3 a) and b) indicate a lace-like network of nanotubes located at the surface of the remaining PLA phase. As the etching solvent extracted only the PCL, the MWCNTs once inside that phase were deposited at the PLA surface during the etching and drying procedure. There are no visible indications for MWCNT localized within the PLA phase. Hence one can conclude that the MWCNTs are mainly located in the PCL phase in which they also were incorporated during the first step of melt mixing.

a)



b)

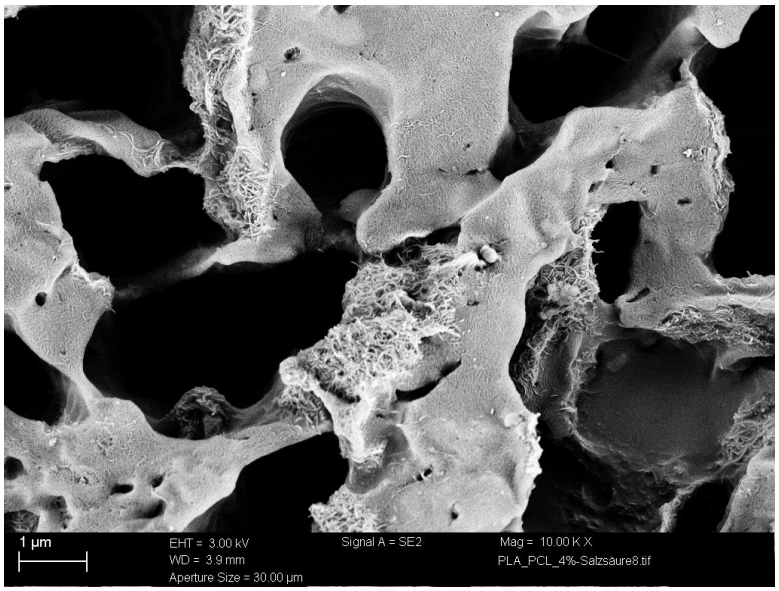


Figure 3. SEM images in different magnifications of the cross section of PCL + 4% MWCNT / PLA = 50/50 wt% fibre, in which the PCL phase was removed by etching with acetic acid at a) low magnification and b) high magnification.

4.4. Structure changes as investigated by WAXD

The changes in the structure of the as-spun PCL + 4% MWCNT / PLA = 50/50 wt% blend fibres during swelling in acetone and ethyl acetate were monitored by WAXD. The diffraction curves of the neat PLA (opaque PLLA and transparent PDLA pellets investigated separately), PCL pellets, and as-spun PCL + 4% MWCNT / PLA = 50/50 wt% multifilament fibres are

presented in Figure 4. The scattering patterns of both, PLLA and PCL homopolymers, revealed semi-crystalline structure whereas the PDLA sample was completely amorphous. The crystal structures of the semi-crystalline samples were consistent with the literature data for PLA [66-68] and PCL [69-71]. The as-spun fibre showed two reflections at 2Θ = 21.4° and 23.7°, which are characteristic for PCL. The PLA phase appears to be completely amorphous. Because of the low content of the MWCNT and/or their poor crystallinity, it could not be detected any crystal reflection corresponding to MWCNT.

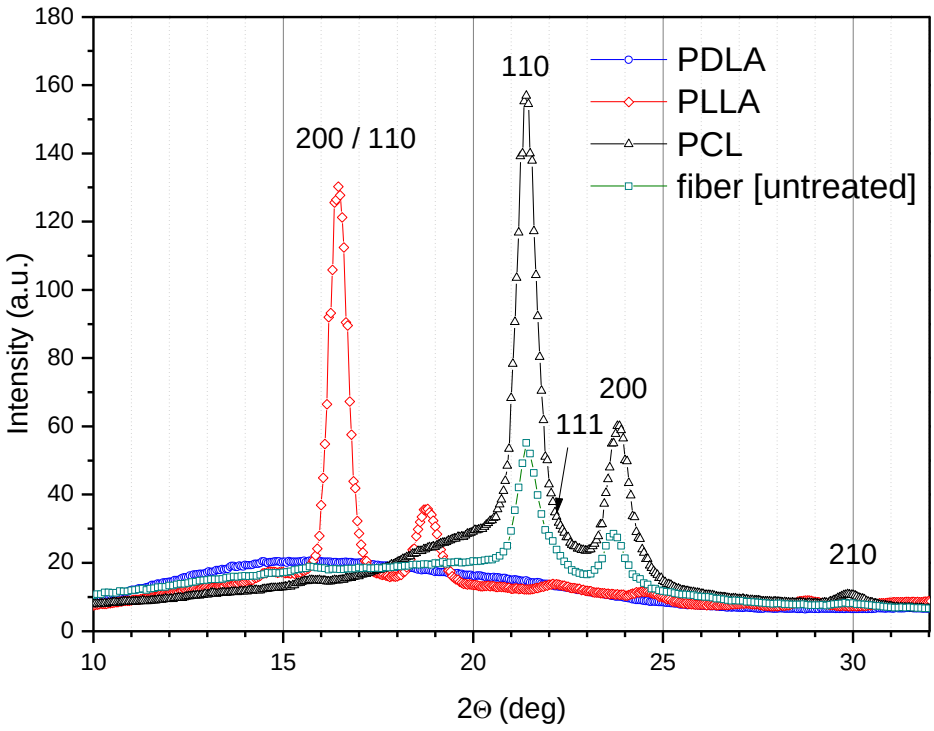


Figure 4. WAXD curves of PDLA, PLLA and PCL homopolymers and PCL + 4 wt% MWCNT / PLA = 50/50 wt% multifilament blend fibres.

Figure 5 shows the scattering patterns of the blend fibre in ethyl acetate for different swelling times. It is well seen that in the first two minutes the intensity of the PLC crystalline peaks drops remarkably. The peak position does not change. This means, that the unit cell does not expand, but the crystal phase transforms to amorphous directly. At the same time, a crystalline peak of PLA occurs and its intensity increases slightly until the last measurement at *t* = 36

min. The amorphisation of PCL was completed in the first 20 minutes. The swelling process in acetone (Figure 6) was very similar to that in ethyl acetate. In order to prove the reversibility of the structure of the as-spun fibre after the solvent contact, two samples were immersed for 6 hours in acetone and ethyl acetate and then dried at ambient conditions for several days. The WAXD curves of the solvent treated fibres are presented in Figure 5 and 6. Both polymers show semi-crystalline features. Hence, the amorphous PLA phase of the melt-spun fibre crystallizes partially in acetone and ethyl acetate and remains semi-crystalline after drying. The semi-crystalline PCL phase of the melt-spun fibre transforms to amorphous in the regarded solvents and returns to semi-crystalline after drying.

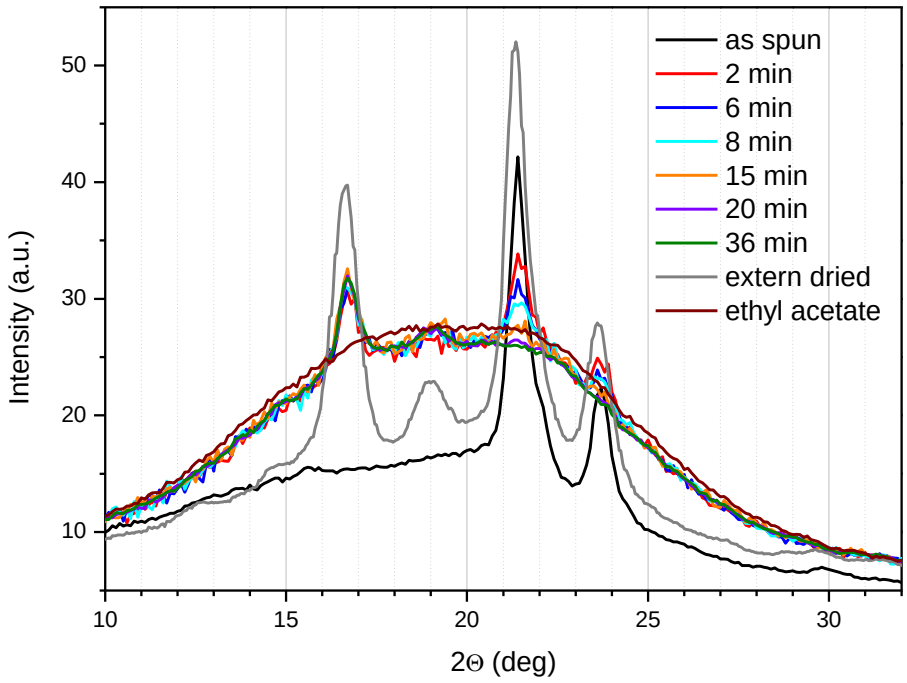


Figure 5. WAXD curves of PCL + 4 wt% MWCNT / PLA = 50/50 wt% multifilament fibres treated in ethyl acetate for different times and dried externally for several days

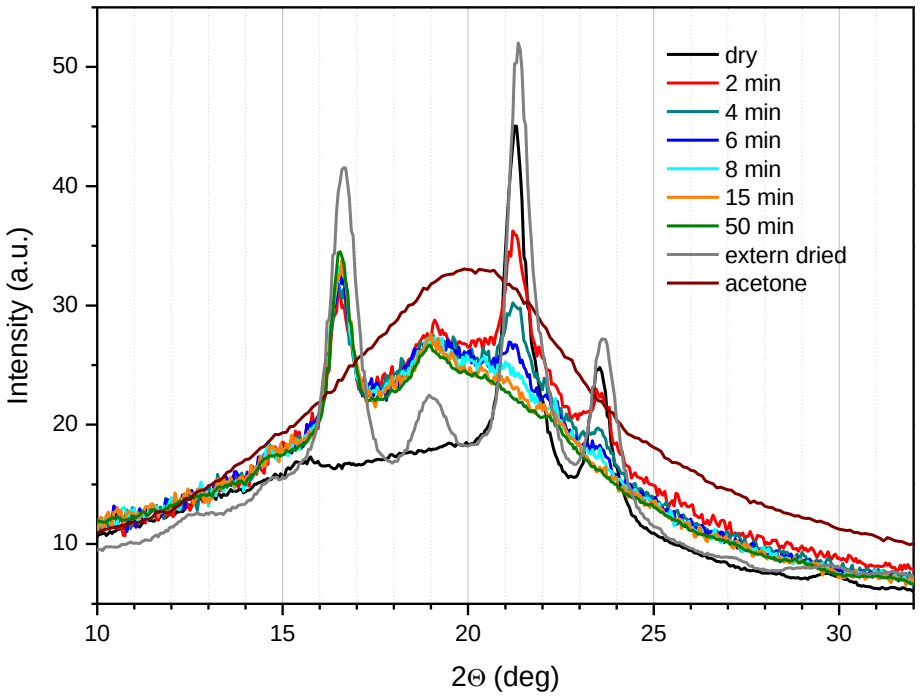


Figure 6. WAXD curves of PCL + 4 wt% MWCNT / PLA = 50/50 wt% multifilament fibres treated in acetone for different times and dried externally for several days.

4.5 Resistance changes in liquid sensing

4.5.1 Multifilament fibres

The initial resistances R_i of four samples with 7 mm length, cut along the same PCL+4% MWCNT / PLA = 50/50 wt% fibre, are listed in Table 4 together with resistance values after 100 s ($R_{rel(100)}$) and 500 s ($R_{rel\ (500)}$) of immersion. The liquid sensing tests with sample 1 and 2 were performed in ethyl acetate, with sample 3 in acetone and with sample 4 in ethanol. As criteria for the liquid sensing response, the resistance change after 100 s ($R_{rel(100)}$) was used as a measure for the response rate and the value at 500 s ($R_{rel(500)}$) as a measure for the amplitude of change, as for the moderate solvents a plateau started to establish after this immersion time. Figure 7 shows the relative resistance change R_{rel} for samples 1 and 2 for 10 immersion / drying cycles in ethyl acetate. Sample 2 was measured twice, as-spun and 13 hours after the first test. The samples reacted immediately after the immersion in ethyl acetate with a steep

rise of the resistance reaching $R_{rel(100)}$ values higher as 16. The $R_{rel(500)}$ values of the 3 samples was in the range between 23 and 35. The drying of the fibre at ambient conditions for 1000 s led to resistance decrease to values slightly higher than the initial ones (due to the remaining solvent in the sample).

The relative resistance change R_{rel} of the PCL+4% MWCNT / PLA = 50/50 wt% fibre immersed in acetone (Figure 8) shows a similar behaviour to R_{rel} in ethyl acetate (Figure 7). As in ethyl acetate, the R_{rel} in acetone increased rapidly and reached a $R_{rel(100)}$ value of 25. The values of $R_{rel(500)}$ are in the range of those in ethyl acetate.

In both solvents the multifilament fibres showed a stable shape indicating that they were resistant against these solvents under the conditions applied. The recovery was fast and after the first cycle the following cycles started at comparable resistance levels.

The relative resistance change R_{rel} of sample 4 in ethanol is presented in Figure 9, as an example for liquid sensing in a poor solvent. The sample response was very slow and $R_{rel(100)}$ was only 0.06. The value of $R_{rel(500)}$ was only 0.2 which is about 2 orders of magnitude lower than that in acetone and ethyl acetate and the plateau of R_{rel} was not reached. Interestingly, even in the drying cycle in the first 750 s an increase in the relative resistance change is observed before R_{rel} starts to decrease.

The relative resistance change $R_{rel(500)}$ increases slightly with each sensing cycle in ethyl acetate and acetone and levels off after some cycles. This behaviour can be explained by the rearrangement of the polymer chains after the immersion in the liquid. As it was mentioned above, the amorphous PLA in the as-spun fibre crystallizes partially in acetone and ethyl acetate and this structure remains after the drying. Kobashi et al. obtained that PLA / MWCNT films treated with ethanol show modest crystallization after drying, which do not reduce the resistance changes upon solvent immersion and drying. However, the isothermal crystallization of the same composite resulting in higher values of crystallinity reduced the starting resistances and the relative resistance change [19]. In the here investigated system, the

crystallization of PLA begins during the swelling and the crystalline peaks after drying are well pronounced (see Figure 5 and 6). The exact degree of crystallinity can not be calculated because of the overlapping of the two WAXD patterns (of PLA and PCL), but the crystallization of PLA during the first cycle does not influence negatively the further liquid sensing properties of the PCL + 4% MWCNT / PLA = 50/50 wt% multifilament fibre. The selective localization of the conductive network of MWCNTs in the PCL phase remaining amorphous during the swelling favours the retaining of the liquid sensing properties. The comparison of the in-situ WAXD curves during the swelling and the liquid sensing results suggests a direct connection of the reversible amorphisation / crystallization (or swelling / drying) processes in the PCL phase and the resistance increase / decrease.

Table 4. The initial resistances R_i of the PCL + 4% MWCNT / PLA = 50/50 wt% multifilament fibre pieces and the relative resistance changes after 100 s ($R_{rel\ (100)}$) and 500s ($R_{rel\ (500)}$) in different solvents and the different cycles. The fibre length was 7 mm.

Sample (solvent)	R_i ***(kΩ)***	$R_{rel\ (100)}$	$R_{rel\ (500)}$
1 (ethyl acetate)	14	20	31-35
2 (ethyl acetate)	12	17	23-28
2 (ethyl acetate) 2nd measurement	20	23	26-30
3 (acetone)	13	25	28-30
4 (ethanol)	12	0.06	0.2

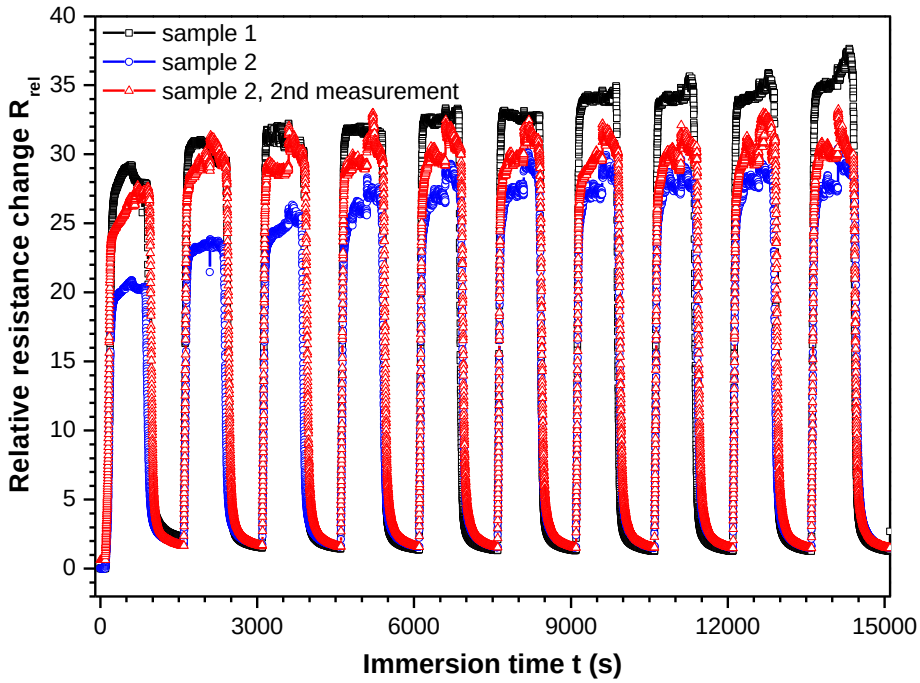


Figure 7. Relative resistance change of PCL+4 wt% MWCNT / PLA = 50/50 wt% multifilament fibres during 10 immersion / drying cycles in ethyl acetate.

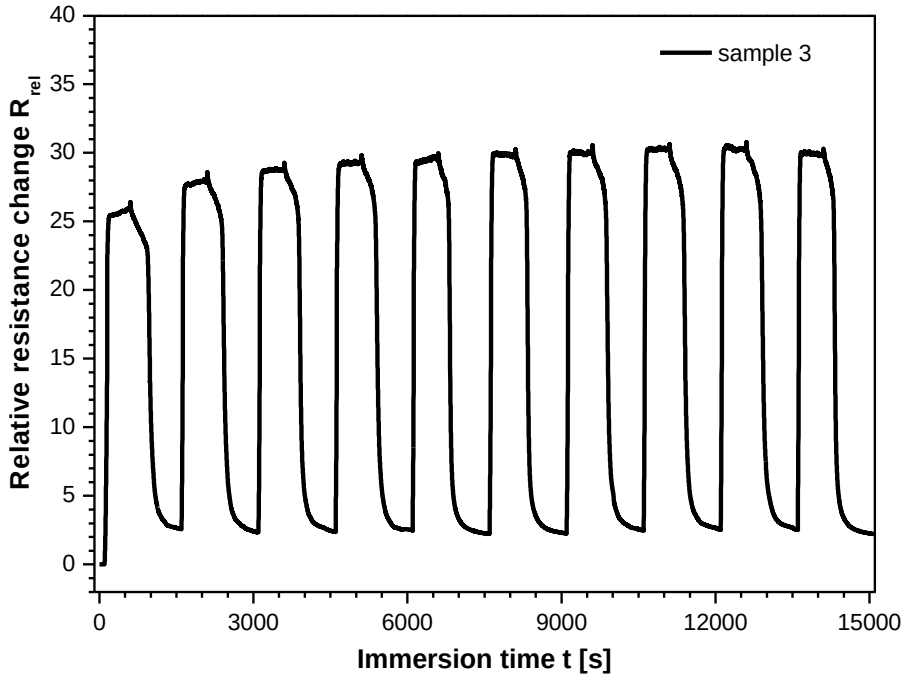


Figure 8. Relative resistance change of PCL + 4 wt% MWCNT / PLA = 50/50 wt% multifilament fibres during 10 immersion / drying cycles in acetone.

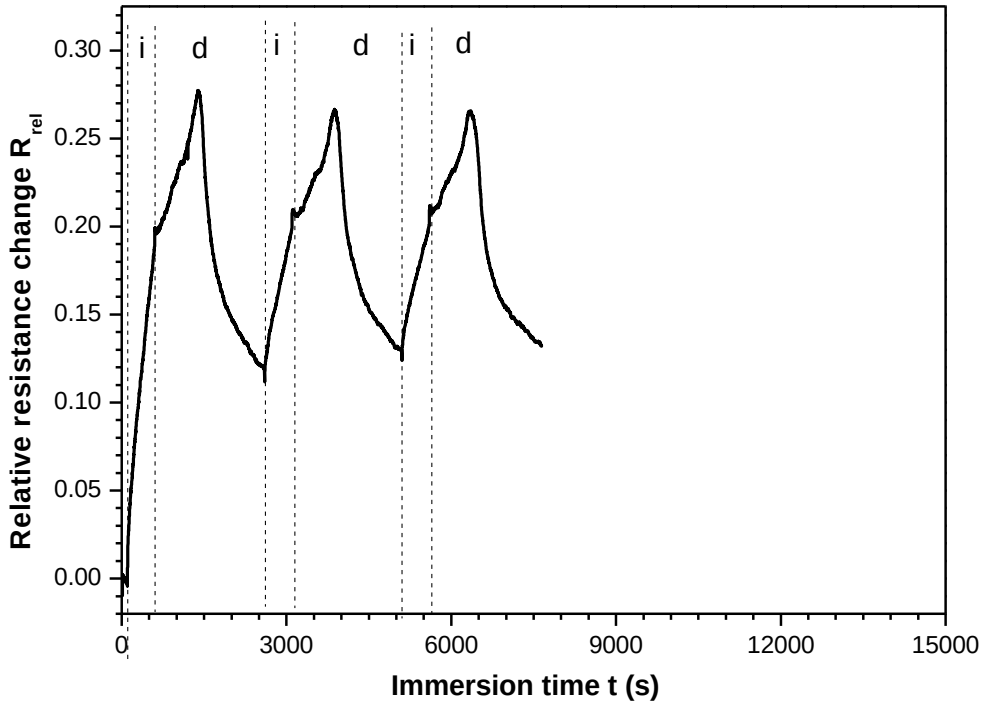


Figure 9. Relative resistance change of PCL + 4 wt% MWCNT / PLA = 50/50 wt% multifilament fibres during 3 immersion (i) / drying (d) cycles in ethanol.

The above presented results show clearly that the relative resistance R_{rel} increases rapidly and reaches very high values after immersion of the sample in moderate solvents (ethyl acetate and acetone). These solvents swell both polymers in the PCL + 4 wt% MWCNT / PLA = 50/50 wt% fibre. In contrast, not much change is observed after immersion in a poor solvent (ethanol) where the polymer swelling is negligible. Some studies showed correlations between the relative resistance change of the samples and the difference in the solubility parameters between the polymer matrix and the solvent [19, 47, 49]. But, also some deviations were reported, especially that solvents with similar solubility parameters resulted in significant differences in the resistance change [48, 49]. In our investigations, the used PCL has a solubility parameter of 19.2 $MPa^{0.5}$ [72], next to it is acetone with 19.9 $MPa^{0.5}$, followed by ethyl acetate with 18.2 $MPa^{0.5}$ and ethanol with 26.5 $MPa^{0.5}$ [73]. In the frame of the error and the different samples tested, the responses of the fibres to ethyl acetate and acetone are the same and that on ethanol is lower. However, a comprehensive study of Villmow et al. [18]

using polycarbonate (PC)/MWCNT based composites as liquid sensing materials revealed that the electrical response characteristics towards 59 test solvents cannot be quantitatively correlated with solubility parameters. The Hansen solubility parameter and in detail the solubility difference between PC and the 59 different solvents and the solvents' molar volume were found to decide whether the composites showed an electrical response when immersed in the solvents and describes the selectivity of composite based sensor materials. However, the electrical response characteristic is determined by the ongoing diffusion processes, which are influenced by the temperature, the solvent molecule size, and the solvent concentration. In addition, the MWCNT content, the initial resistances and the geometrical details of the samples influence the response characteristics which can be described using an empirical model as shown for PC/MWCNT composites [21].

Comparing the liquid sensing investigations on PLA/MWCNT films and MWCNT mats, Kobashi et al. [19] connected the relative resistance change in PLA/MWCNT composites with the swelling of the polymer matrix combined with the direct interactions between solvent molecules and the nanotubes.

Using several polymer/carbon black conductive composites, Belmares et al. built an electronic nose that relied on changes in electric resistivity of the polymer film as a function of the amount of swelling due to the contact with solvent vapours [74]. They correlated the relative resistance change with the Hansen components of the cohesive energy of the polymer and the solvent as well as with the molar volume of the solvent.

In studies on polymer / MWCNT composites as vapour sensors an inverse relationship between the relative resistance amplitude and the Flory-Huggins interaction parameter χ_{12} between the polymer matrix and the vapour [20, 25] was shown, however only a limited number of solvents was used and even here exceptions were found [25].

4.5.2 Textiles

The liquid sensing answer, i.e. the relative resistance change of the PCL + 4 wt% MWCNT / PLA = 50/50 textile samples on ethyl acetate and acetone is presented in Figure 10 and Figure 11, respectively. The samples show a very clear reaction on the wetting with both solvents whereas the maximum amplitude is slightly lower in acetone. The maximum relative resistance change in the range of 3-5 is one order of magnitude lower in comparison with that of the single PCL + 4 wt% MWCNT / PLA = 50/50 multifilament. However, the difference in the measuring procedures must be taken in account; the single multifilament was left to swell for a 500 s in the solvent and a textile sample was only wetted with 2 ml solvent. The drying (solvent evaporation) begins immediately after the dropping; however the swelling of the PCL + 4 wt% MWCNT / PLA = 50/50 fibres continues approx. 200 s for the first cycle and 130 - 150 s for the next ones. The very slow drying cotton fibres act probably as a solvent buffer and extends the swelling time of the PCL + 4 wt% MWCNT / PLA = 50/50 blend multifilaments.

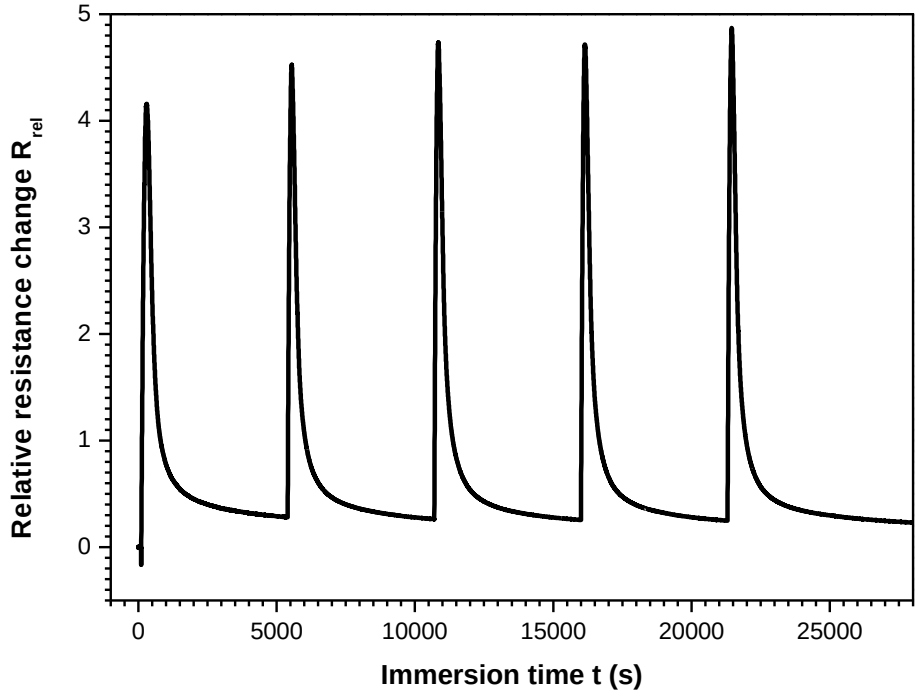


Figure 10. Relative resistance change on PCL + 4 wt% MWCNT / PLA = 50/50 wt% textile upon 2 ml ethyl acetate for 5 wettings at *t* = 100 s, 5400 s, 10700 s, 16000 s and 21300 s.

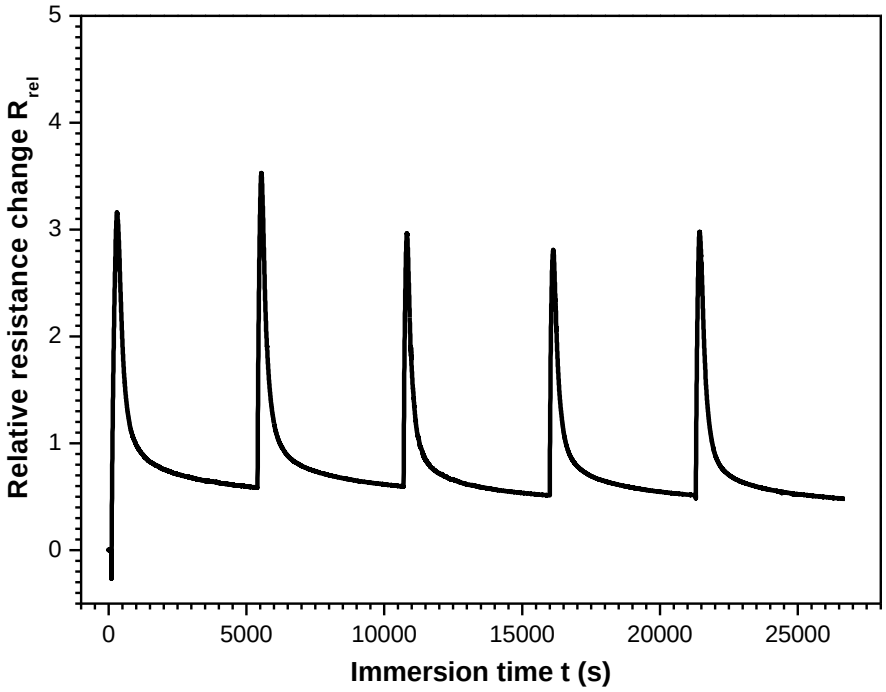


Figure 11. Relative resistance change on PCL + 4 wt% MWCNT / PLA = 50/50 wt% textile upon 2 ml acetone for 5 wettings at *t* = 100 s, 5400 s, 10700 s, 16000 s and 21300 s.

5. Summary

Conductive PCL + 4 wt% MWCNT / PLA = 50/50 wt% blend multifilament fibres were melt-spun for producing a textile sensor for liquids. The fibres were tested for liquid sensing in two moderate solvents, namely ethyl acetate and acetone, and one poor solvent which was ethanol. The liquid sensing responses of the sample on ethyl acetate and acetone were fast with relative resistance changes after 100s higher than 16 and showed very high amplitudes (relative resistance changes after 500s higher than 32). In addition, fast and nearly complete recovery (within 1000 s) was observed and the electrical responses were well reproducible in the studied 10 cycles. At the same time, the fibres were resistant against these solvents. The response on ethanol was less pronounced, even if the studied second and third cycles were

also reproducible. The relative resistance change was very slow (only 0.06 after 100s) and the amplitude reached after 500 s of solvent immersion was low (relative resistance change of only 0.2).

It was found that PLA crystallizes during the immersion process, PCL swells fully and all the crystalline domains transform to amorphous ones. The crystallization of PLA does not influence negatively the liquid sensing properties which has to be assigned to the finding confirmed by SEM investigations that the MWCNT are predominantly localised in the PCL phase.

In conclusion, PCL + 4% MWCNT / PLA = 50/50 wt% multifilament fibres are very promising materials for building a textile sensor for two widely used solvents – ethyl acetate and acetone.

In the final step, a textile based on those fibres was prepared and its sensing behaviour was investigated on ethyl acetate and acetone clearly showing that such textiles are suitable to detect these solvents. Maximum resistance changes between 3 and 5 were observed after wetting the textile with a defined amount of the solvents.

In conclusion, PCL + 4% MWCNT / PLA = 50/50 wt% multifilament fibres and textiles made therefrom are very promising materials for building a textile sensor for two widely used solvents, namely ethyl acetate and acetone.

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Vitae

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