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PII: S0266-3538(11)00193-X
DOI: 10.1016/j.compscitech.2011.05.019
Reference: CSTE 4999

To appear in: *Composites Science and Technology*

Received Date: 4 August 2010
Revised Date: 23 May 2011
Accepted Date: 28 May 2011

Please cite this article as: Pötschke, P., Kobashi, K., Villmow, T., Andres, T., Paiva, M.C., Covas, J.A., Liquid sensing properties of melt processed polypropylene/poly(ε-caprolactone) blends containing multiwalled carbon nanotubes, *Composites Science and Technology* (2011), doi: 10.1016/j.compscitech.2011.05.019

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Liquid sensing properties of melt processed polypropylene/poly(ε-caprolactone) blends containing multiwalled carbon nanotubes

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Abstract

The sensing properties of polypropylene (PP)/poly(ε-caprolactone) (PCL) blends containing multiwalled carbon nanotubes (MWNT) were studied in terms of their electrical resistance change in presence of liquids (solvents). The preparation of co-continuous blends based on the double percolation concept was done by melt mixing of electrically conductive PCL composites containing 3 wt.% MWNT and neat PP in ratios of 30:70, 40:60, and 50:50. The electrical resistance change of the PCL-MWNT composites and blends was monitored in a solvent immersion/drying cycle. Various solvents, such as n-hexane, ethanol, methanol, water, toluene, chloroform, and tetrahydrofuran were successfully detected, yielding different responses and reversibility of the resistance changes.

PP and PCL were tested separately for solvent sorption using ethanol and n-hexane, both showing a low sorption of n-hexane. Ethanol sorption was large for PCL and almost absent for PP. The 50/50 blend composites with 3 wt.% MWNT in the PCL phase presented larger resistance changes for n-hexane, showing larger sensing ability for this solvent compared to PCL composites with 1 and 3 wt.% loadings. The opposite response was observed for immersion in ethanol where the PCL-MWNT composites showed larger changes than the blends. As the ratio of the conductive PCL phase over PP in the blend composition (i.e., the overall MWNT content) decreased, larger resistance changes were observed. The liquid sensing properties of compression-moulded disks and melt-drawn filaments were compared indicating higher responses for the disks.

Keywords: A. Carbon nanotubes, Nano composites, Polymer-matrix composites (PMCs);

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B. Electrical properties; E. Melt-spinning

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1. Introduction

Carbon nanotube (CNT) based electrically conductive polymer composites (CPCs) offer a broad range of opportunities because of their unique property profile with low specific gravity [1] in combination with relative good processability and improvements in mechanical and thermal properties. In recent years, such composites were also investigated as sensor materials to detect various external stimuli. Next to CPCs based on carbon black (CB) or other conductive fillers, sensor materials based on carbon nanotube (CNT)/polymer composites were shown to respond in terms of their electrical properties to external stimuli including bio molecules [2-4], gases [5-15], vapours [5, 16-21], liquids [22-24], taste components [25], mechanical stress [2, 5, 26, 27], temperature [7, 8, 26, 28] and pH [29].

In general, CPCs are seen as promising candidates for liquid sensing materials to detect, e.g., solvent leakages. Whereas a lot of knowledge has been generated for CB based composites and blends, not much is reported about liquid sensor materials containing CNTs. As CNT based composites have lower percolation thresholds as compared to those based on CB, composites and blends with lower filling grade can be used for sensing purposes. In addition, with the intention to use melt-spun fibers for textiles acting as liquid sensor materials, there are advantages of CNTs versus CB. The ability to draw fibers from carbon black filled systems is very limited, while with nanotubes the processability is much better. Thus, it seems to be interesting also to investigate composites and blends based on CNTs for liquid sensing purposes.

For melt-processed biphasic polymer/ CB composites, Narkis et al. reported the liquid sensing behaviour of [30-34]. In the immiscible polymer blends containing CB, like PP/PA6/CB, HIPS/EVA/CB, and PP/TPU/CB, the liquid sensing behaviours depended on their components, composition, and composite morphologies, which could be influenced by the melt-processing method and mixing conditions. It was suggested that the solvent sorption and resultant sensing behaviours were also influenced by the interface between the polymer blend phases.

Sumita et al. first introduced the concept of “double percolation” on CB-filled blends [35]. The electrical conductivity of these blends is achieved by the electrical percolation of the filler in one phase and the co-continuity of this phase in the blend. The use of carbon-based fillers in polymer blends as liquid sensing materials is attractive due to the almost endless variety of polymer blend

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structures [36]. Numerous publications describe the electrical and mechanical properties of polymer blends containing CNTs (mainly multiwalled CNTs, MWNT) produced by melt processing – an advantageous method in the context of industrial scale-up. PC/PE/MWNT blend composites with double percolation resulted in much lower electrical percolation than monophasic PC-MWNT composites [38, 39]. It was reported that CNT-filled PA6/ABS blends with double percolation possess better mechanical properties than the equivalent ones filled with CB [40]. PET/PVDF/CNT composites exhibited better electrical and mechanical properties than CNT-filled PET with the same nanotube loading [41, 42]. In most studies a localisation of nanotubes in the thermodynamically preferred phase was observed as discussed e.g. in a recent publication regarding the localisation of CNT in highly compatible but immiscible blends of polycarbonate (PC) and styrene-acrylonitrile (SAN) [37]. It was shown, that the CNTs are preferentially located in the PC phase even if the SAN phase was initially filled with the CNTs which can explained in first approximation using the concept of the wetting coefficient.

To our knowledge the liquid sensing behaviour of polymer blends containing CNTs is not yet described in literature, even if for monophasic systems some results are reported. PLA/MWNT composite films were investigated at nanotube loadings near to the electrical percolation threshold and the sensing mechanism was investigated [22, 23]. It was shown that the nanotube content and the PLA crystallinity have a significant effect on the sensing properties of the composites. In addition, melt-spun fibres of polylactide (PLA)/MWNT composites were studied indicating a dependence of the liquid sensing properties on the take-up velocity and the resulting nanotubes orientation during spinning [24]. Before studying these materials, the melt processing conditions using twin-screw extrusion were optimised in order to achieve a high level of nanotube dispersion in PLA and PCL [43, 44]. For both matrices electrical percolation on compression moulded disks was obtained below 0.5 wt% MWNT content. Based on results for the immersion of polycarbonate-MWNT composites into various solvents, Villmow et al. [45] derived a model allowing the calculation of the time depending relative resistance change considering several factors like diffusion parameters of the solvents into the matrix, composite characteristics like starting resistivity, and geometrical values of the samples.

The present work focuses on the liquid sensing behaviour of PCL-MWNT/ PP blends with double percolation structures which are manufactured by melt processing. The nanotubes were first mixed into PCL and according to the concept of the wetting coefficient they should remain in this phase after mixing with PP. This blend system was chosen as it provides the presence of two polymer phases having completely different solubility behaviours. Whereas for PCL good

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swelling in most solvents at room temperature is expected, PP is much more difficult to swell. Thus, PCL with MWNT is the sensing phase whereas the PP phase mechanically stabilizes the co-continuous blend systems. The sensing properties were studied in a solvent immersion/drying cycle. Both poor and good solvents of PCL were used, according to the associated solubility parameters. A comparison of the sensing properties of composites shaped as pressed disks and as melt-drawn filaments was made. The influences of blend composition and overall nanotube content on the sensing capacity were investigated. Finally, the sensing capacity of the blends was compared with that of the conductive PCL/MWNT material.

2. Experimental

2.1 Materials, composite and sample preparation

PCL (CAPA 6800, Perstorp) is a biodegradable polymer with a relatively low melting temperature (about 60°C) and a glass transition temperature of about -60°C. The PP (HF445FB, Borealis) is a spinning grade, which was expected to provide easy processing of the PP/PCL blends. The PCL was dried in a vacuum oven at 40°C for 24 h before processing and was then melt-mixed with Nanocyl® NC 7000 (Nanocyl S.A., Sambreville,, Belgium). This grade represents multiwalled carbon nanotubes produced via the CVD process, having according to the provider a purity of 90 %, a typical diameter of 9.5 nm, and an average length of 1.5 µm. Compounding was performed using a Berstorff ZE 25 co-rotating twin screw extruder. A masterbatch with 7.5 wt% MWNT content was first produced and then subsequently diluted to composites containing 0.5, 0.75, 1.0, 1.5, 2.0, 3.0 wt% MWNT. The compounding was done on basis of recent investigations [43] using a distributive screw configuration, a rotation speed of 500 min^{-1}, a throughput of 5 kg/h, and a mean barrel temperature of 190°C.

The final production of blends based on PCL with 3 wt.% MWNT and PP in the ratios 30:70, 40:60 and 50:50 wt% was done using the same twin-screw extruder with slightly changed processing conditions. Instead of a distributive screw configuration, a standard compounding screw with mixing and kneading elements was used. Detailed information about the screw design can be found in a recent publication [44]. While the throughput was kept constant at 5 kg/h, the rotation speed was lowered to 300 rpm, and the processing temperature was slightly increased to 200°C.

Compression moulding of the materials was performed in a PW 40EH Press (Weber, Germany) under constant pressing conditions (1 min under 15 kN at 200°C, after pre-heating during 3 min), to obtain disks with a diameter of 60 mm and a thickness of 0.5 mm.

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The PCL-3 wt.% MWNT/PP = 50/50 blend composite was in addition processed using a prototype monofilament extrusion line consisting of a Periplast (Portugal) single screw extruder (screw diameter 25 mm, Meillefer-type screw) coupled to a two-hole filament die and downstream equipment comprising a water cooling tank, first set of 5 pulling rolls, 1.1 meter long oven (for filament orientation), second set of 5 pulling rolls (for drawing the filaments at the required stretching ratio) and constant tension winder. The available second oven and third set of pulling rolls (for relaxation or, conversely, further orientation purposes) was not used in this work. The barrel of the extruder was set at 180/185/195/210ºC from hopper to die, while the screw rotated at 10 rpm. The orientation oven was kept at 150ºC. Although filaments with draw-ratios from 1.4 up to 10.5 were produced, only those obtained with the lower draw ratio showed adequate sensing properties.

2.2 Material characterization

2.2.1 Electrical resistance

The electrical resistance of compression-moulded disks was measured using two devices. Disks having an electrical resistance above 10^7 Ω were analysed by means of a Keithley Test Fixture 8009 in combination with a Keithley Multimeter 6517A. In case of lower resistances, small strips were cut from the disks which were analysed using a self-made resistivity measurement device (4-point test fixtures, gold contact wires with a distance of 20 mm between the source electrodes and 10 mm between the measuring electrodes) in combination with a Keithley Electrometer DMM 2000 (measurement range from 10^{-3} to 10^7 Ω).

2.2.2 Morphology

The morphology of the MWNT filled polymer blends was observed using a scanning electron microscope Ultra 55 plus (Carl Zeiss SMT) on selectively etched cuts of extruded granules. The PCL part was removed by dissolving in chloroform at room temperature for 24 h. The melt drawn filaments were observed using light transmission optical microscopy (Olympus BH2) on 5 µm thick sections prepared along and perpendicular to the filament direction. The sections and the surfaces were cut with a JUNG RM 2055 microtome (Leica, Germany) at room temperature using a histo diamond knife with a cut angle 45° (Diatome, Switzerland).

2.2.3 Liquid sensing

The liquid sensing properties of the composites were examined with various solvents at different MWNT loadings. U-shaped samples were cut from the compression-moulded disks, the electrodes being connected to both ends and coated with a silver paint [22, 45]. Portions of the

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melt-drawn filaments with 5.5 cm length were clamped by set screws to copper electrodes, which were sealed with airproof poly(tetrafluoroethylene) caps to prevent the solvent level from rising to the electrodes during immersion [24]. Only the filament was in direct contact with the solvents, while the contact point between the filament and the electrode remained dry. For all liquid sensing tests, the immersed length of the filaments was 10 mm.

The samples were immersed in solvent kept at 30°C (in an oil bath) for a given period of time, then removed and left to dry in air. The solvents used were n-hexane, toluene, chloroform, tetrahydrofuran, ethanol, methanol (all purchased from Acros Organics), and distilled water. The solvent drops remaining on the samples were wiped using a tissue off at the beginning of the drying step. Sample swelling and shrinkage could be observed when using solvents with solubility parameters similar to that of PCL (toluene, chloroform, tetrahydrofuran).

The electrical resistance changes of the samples were monitored with a Keithley 2001 multimeter (measurement range from 10^{-6} to 10^{9} Ω) with a resolution of one second. To facilitate the comparison between samples, the initial resistance at the beginning of the experiment (R_i) and that at time t (R) were taken into account. A relative resistance change (R_{rel}) was calculated according to **Equation 1** [22-24].

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

2.2.4 Sorption and desorption

Since the changes in the electrical resistance of the composites during solvent immersion and drying were expected to arise from solvent sorption and desorption by the composite, these processes were studied on compression-moulded disks of neat PCL, PP and composites. The disks were dried under vacuum for at least 18 h at 40°C prior to the immersion in the solvent. In the case of the sorption experiments, the disks were immersed in solvent kept at 30°C for a given period of time, then removed to weigh the solvent uptake within 20-30 seconds. Different disks were used for different sorption times. The remaining solvent drops on the disks were wiped off. For the desorption experiments, the disks were first immersed in the solvent for 60 min, and then removed to be dried in air for 60 min. The weight loss evolution monitoring was started immediately after wiping off all excess solvent present on the disks surface. The solvent content, S, at time t was calculated by taking into account the weight at that time (m_t) and the initial weight (m_i) (**Equation 2**) [22, 23].

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$$S = \frac{m_t - m_i}{m_t} \cdot 100\% \qquad \textbf{Equation 2}$$

After the sorption/desorption process, followed by vacuum drying of the tested disks, negligible weight losses were measured, thus indicating that polymer dissolution had hardly occurred.

3. Results and Discussion

3.1. MWNT dispersion in PCL-based composites and morphology of PCL- MWNT/PP blends

The formation of a conductive network in the polymer matrix is the key for liquid sensing since the responses to liquid contact result from changes of its electrical properties due to swelling of the polymer matrix. As seen in **Figure 1**, the electrical percolation threshold of PCL-MWNT is observed below 0.5 wt.%. Morphological observations showed good MWNT dispersion and distribution in the polymer matrix, thus yielding the formation of a conductive MWNT network structure at such low MWNT contents [43].

With the aim of producing co-continuous blends with double percolation, the PCL-3.0 wt% MWNT composite was selected as being in the well-percolated range and was melt-mixed with PP at different compositions. The electrical resistivities of the produced PCL-MWNT/PP blends are shown in Figure 1. Interestingly, in contrast to the expectations the blends show slightly higher resistivity values as compared to PCL composites with the same loading but are all electrically conducting confirming the continuity of the filled PCL phase. The higher resistivities may be a hint for nanotube shortening during the blending extrusion step [46-49]. The co-continuous structure of the blends could be confirmed by SEM on selectively etched sample surfaces (**Figure 2)** where the remaining continuous PP phase is seen. At higher magnification the nanotubes are seen as remains on the surface of the PP phase and between the PP phase ligaments. This indicates that the nanotubes were localized before etching in the PCL phase, in which they also were introduced first.

3.2. Sensing behaviour of PCL-MWNT (compression-moulded disks)

In order to gain a global understanding of the liquid sensing behaviour of polymer blends with MWNTs, the liquid sensing performance of the monophasic PCL-MWNT composite - which corresponds to the electrically conductive phase of the blends studied - was investigated first, using poor and good solvents. Two materials tend to be miscible if the difference between their solubility parameters, δ, is small. Thus, according to their Hansen solubility parameters (HSP,

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[46]) shown in **Table 1**, n-hexane, ethanol, methanol, and water can be regarded as poor solvents of PCL, whereas toluene, chloroform, and tetrahydrofuran are good solvents.

The sensing properties of PCL/MWNT disks were studied at different nanotube loadings during 10 min immersion in the solvents and 10 min drying in air. As seen in **Figure 3**, with decreasing nanotube loading the relative resistance changes R_{rel} during immersion become larger and the following ranking of R_{rel} is observed: water < ethanol < methanol. The differences between methanol and ethanol are very small at the highest MWNT loading. These results support the hypothesis [22] that the partial disconnection of the conductive MWNT network occurs readily at loadings near the electrical percolation threshold, due to the formation of less dense nanotube networks.

The relationship between sorbed solvent content and resulting resistance changes during immersion in poor solvents was investigated for the PCL-3.0 wt.% MWNT composite (**Figure 4**). The two sorption times of 10 and 360 min induce the same trend of sorbed solvent content (water < ethanol < methanol), which is identical to the ranking of resistance changes. As more solvent molecules are sorbed into the composite, the larger resistance changes are measured. However, the difference in solubility parameters of PCL and methanol is a little larger than that between PCL and ethanol (**Table 1**). Since methanol and ethanol are chemically similar, the enhanced response measured for the composite immersed in methanol may be due to the smaller solvent molecular size that may lead to higher solvent sorption relative to ethanol. Interestingly, despite for water the composites with CNTs have lower solvent uptakes than the pure PCL especially evident at the longer immersion time of 360 min. This indicates a nanotube blocking effect against the penetration of the solvent molecules, as proposed recently [23, 45].

The global liquid sensing properties of PCL-3.0 wt.% MWNT composites were studied after 30 s immersion in good solvents and 10 min immersion in poor solvents (**Figure 5)**. Samples were visibly swollen after immersion in the good solvents. Fig. 6A shows that solvents with δ values close to that of PCL resulted in the largest R_{rel}. Probably, partial disconnection of the conductive MWNT network in the polymer occurred more extensively when using a good solvent as the swelling of the polymer matrix is much more pronounced. Good reversibility of the resistance values during drying was obtained for poor solvents. In the case of good solvents, the resistance decreased only slightly during drying and even further increased for chloroform.

3.3. Sensing behaviour of PCL-MWNT/PP blends (compression-moulded disks)

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The experimental procedure adopted above to study the liquid sensing of PCL-MWNT composites was adapted to PCL-MWNT/PP = 50/50 wt% blends. The relative resistance changes, R_{rel}, are shown in **Figure 6**, while the R_{rel} values after 30 s of solvent immersion are plotted against the solubility parameters of the various solvents, δ, in **Figure 7**. As before, the larger R_{rel} were obtained with solvents having δ values closer to that of PCL. In opposition to PCL/MWNT composites, in the blends the R_{rel} of n-hexane is larger than those of ethanol and methanol. Relatively good reversibility of the resistance values during drying was observed for all solvents. When good solvents for PCL were used (toluene, chloroform, and tetrahydrofuran), polymer swelling was not visible, again unlike what happened for PCL/MWNT composites. However, after immersion in the solvents, the surface of the sample became grey, indicating beginning dissolution of the PCL phase. Apparently, swelling was constrained by the PP phase of the co-continuous blend, which presented much lower solvent sorption.

The effect of the blend composition on the liquid sensing properties was investigated and PCL-3 wt.% MWNT:PP ratios of 30:70, 40:60, and 50:50 (corresponding to an overall MWNT content in the composites of 0.90, 1.05, and 1.50 wt.%, respectively). Ethanol, methanol, and water were selected as poor solvents for both PCL and PP. A cycle of 10 minutes immersion and 10 minutes drying was applied. The absolute resistance changes after 10 min (R_{max} - R_i) are summarised in **Figure 08**. As the proportion of MWNT-filled PCL to PP decreases or, equivalently, the overall MWNT content decreases, the initial resistance values of the composites become larger, and higher resistance increases on solvent contact are detected. This is in agreement with the results obtained for PCL/MWNT at different nanotube loadings (**Figure 3**). The effect of the blend composition on R_{rel} (not shown here) is relatively small, which may imply that the MWNT network density in the PCL phase remains approximately the same regardless of the PCL/PP proportion.

In the blends, a lower solvent uptake than in the PCL- 3 wt.% MWNT composites was found indicating a hindering of solvent uptake due to the co-continuous structure. As PP hardly sorbs any polar solvents (ethanol, methanol and water) the solvent uptake only occurs into the swellable PCL paths reaching the surface of the sample under immersion. The solvent sorption of all disks follows the ranking: water < ethanol < methanol (**Figure 5**), which partly supports the data on the resistance changes of the blend composite. The change of the MWNT network within the blend upon contact with water was found to be smaller as it was the water uptake as compared to ethanol and methanol having much higher resistance changes.

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3.4. Sensing behaviour of PCL-MWNT/PP blends vs. PCL-MWNT composites (compression-moulded disks)

The sensing behaviour of PCL-3 wt% MWNT/PP blends (with 1.05 wt% overall MWNT content) was compared with those of PCL with 1.0 and 3.0 wt% MWNT content for two different solvents with different characteristics. **Figures 9 and 10** show in addition to the relative resistance change R_{rel} the solvent sorption/desorption behaviour upon immersion in ethanol and n-hexane, respectively and subsequent drying in air.

Selective penetration of ethanol (a poor solvent for both PCL and PP) in the PCL phase is anticipated, since PP hardly sorbs ethanol. The resistance and the sorbed solvent content increased gradually with immersion time (Figure 10). After 1 hour immersion, the solvent uptake reached ca. 0.11, 0.1, and 0.05 mol.% for PCL-1.0 wt.% MWNT, PCL-3.0 wt.% MWNT, and the blend composite, respectively. The sorbed ethanol content of the blend was approximately half of that for PCL-3.0 wt.% MWNT, as expected. This could also mean that the interface between the PCL and PP phases does not play an important role in the ethanol penetration in the blend. During drying, the resistance decreases following the decrease in the content of the sorbed solvent and this fall is being steeper for the PCL-3.0 wt% MWNT than for the blends. The co-continuous blend structure appears to slow down the solvent desorption due to its tortuous pathways. The R_{rel} values after 1 hour immersion were largest for PCL-1.0 wt.% MWNT followed by PCL-3.0 wt.% MWNT and the PCL-3 wt.% CNT/PP blend. However, in the early stages of solvent immersion, the blend yielded the largest R_{rel}, i.e. the fastest response despite a smaller solvent uptake. Since the ethanol molecules mostly penetrate the amorphous regions of the PCL phase, the efficiency to increase distances between neighboured nanotubes within the network seems to be higher than that for PCL- 3 wt.% MWNT composites. Nevertheless, the blend composite's resistance increase rate reduces significantly with immersion time.

N-hexane is expected to penetrate more into PP than in the PCL phase, due to its nonpolarity. The resistance and the sorbed solvent contents increase gradually with immersion time (Figure 11). The resistance change R_{rel} of both PCL-MWNT composites is lower than that upon immersion in ethanol due to the lower sorbed solvent content. Whereas the resistance variation for the composites immersed in ethanol (poor solvent for PP) increase in the order: blend < PCL-1.0 wt.% MWNT < PCL-3.0 wt.% MWNT, in n-hexane (better solvent for PP) the order is reversed: the blend shows the highest resistance change as well as solvent uptake.

With the aim of elucidating the sorption/desorption behaviour of the two blend phases with ethanol and n-hexane, similar control experiments were performed with PCL and PP disks

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(**Figure 11**) without CNTs. In the case of ethanol, the sorbed solvent content on PCL reached ca. 0.11 mol.% after 10 minutes immersion, whereas PP hardly sorbed the solvent. This demonstrates that ethanol molecules are selectively sorbed by the PCL phase. Both PP and PCL sorbed n-hexane, but the content was larger for PP (0.05 versus 0.02 mol.%). The blend sorbs ethanol through PCL only, while n-hexane is sorbed by the two phases. In the second case, swelling of both the PCL and PP phases is caused by solvent penetration, resulting in an extensive disconnection of the MWNT network. In turn, this causes a relative resistance change larger than that measured for both PCL-MWNT composites.

3.5. Sensing capacity of PCL-MWNT/PP disks and filaments

The influence of processing conditions and blend morphology on the liquid sensing properties were investigated by comparing the performance of compression-moulded disks and melt-drawn filaments prepared from the same PCL-3 wt.% MWNT/PP = 50/50 blend granules. The average diameter of the filaments prepared using a draw ratio of 1.4 was 1.0 mm and their electrical resistance prior to solvent contact was approximately 515 Ωcm, i.e., a higher value than that of the pressed disks (9 Ωcm). Thus, it appears that even a small drawing ratio caused an increase of the electrical resistance as compared to compression moulding which is in agreement with findings in the literature (e.g. [47]). The strong alignment of the co-continuous structure in the melt-drawn filaments can be seen in **Figure 12**, in which along the filament direction long fibrils are visible which appear perpendicular to the draw directions as elongated black, nanotubes filled, areas within a white appearing (unfilled) matrix. Such observations are typical for highly elongated co-continuous structures, as demonstrated e.g. in [36, 48] but also could represent fibrillar morphologies.

The relative resistance changes upon immersion of the filaments in different poor solvents are presented in **Figure 13**. The comparison with the corresponding data for the disks (**Figure 6**) shows that the filaments generally show lower relative resistance changes after 10 min of immersion in n-hexane, ethanol, methanol, and water. The highest values and the lowest difference to the disks were observed for n-hexane, where after 10 min values of 0.48 and 0.36 were reached for melt drawn filaments and compression-moulded disks, respectively. It should be noted that the filaments have a surface area of 31.4 mm² in contact with the solvent, while the disks (U-shaped samples) have 91.0 mm². As the volumes of the fraction of sample immersed in solvent are 7.9 mm^3 (filaments) and 19.5 mm^3 (U-shaped samples), the surface area to volume ratios are nearly equivalent, 4.0 and 4.7, respectively. Therefore, the differences in R_{rel} must

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result from different blend morphologies combined with differing MWNT network structures in disks and filaments. The formation of the MWNT network depends on the nanotube aspect ratio, which determines the nanotube load necessary to attain the percolation threshold but also on the orientation of the nanotubes within the structure. It has been reported that melt mixing under high shear can result in significant shortening of the CNTs [49-52]. For CNT-reinforced polymer nanocomposites, correlations between percolation threshold, dispersion state, and carbon nanotubes aspect ratio have been discussed in literature [53]. In the present study, the preparation of melt-drawn filaments of PCL-3 wt.% MWNT/PP blends includes an additional melt processing step by using a single-screw extruder and forcing the composite trough the filament forming die. This may lead to an additional shortening as compared to that may have already occurred during composite preparation and melt blending. However, also the thermo-mechanical conditions used in the preparation of the disks and filaments were different which could lead to different states of the secondary agglomeration of nanotubes due to different annealing and cooling times after different shear expositions [54]. As another influence, the alignment of the nanotubes which may be assumed according to the light microscopy observation of an alignment of the blend phases can lead to reduced nanotubes contacts and thus, to higher resistivity values in the melt-drawn filaments [47]. The degree of co-continuity of the blend also could influence the resistance of the composite. However, the 50/50 wt.% blend is characterized by a well-established co-continuous structure, and its existence may be assumed also in the highly stretched filaments, so that the influence of this factor should be minor.

4. Summary and Conclusions

The liquid sensing properties of polymer blends based on PCL filled with MWNT and PP were investigated. The sensing experiments consisted in the immersion in solvent of disks or melt-drawn filaments, followed by drying in air, and simultaneous measurements of the electrical response in a range of solvents whereas n-hexane, ethanol, methanol, water, toluene, chloroform, and tetrahydrofuran were successfully detected. The main conclusions may be summarized as follows:

- The percolation threshold for PCL-MWNT was below 0.5 wt%. The PCL-3 wt.% MWNT/PP blends presented co-continuous structure over a broad range of blend composition (30/70 to 50/50) and were conductive in that range. The nanotubes were localized selectively in the PCL phase in which they were initially compounded.

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- PCL composites with 0.5 to 3 wt.% MWNT content were tested for resistance variation during immersion in a range of poor and good solvents. Composites with lower MWNT content and thus less dense nanotube network presented larger resistance increases during immersion in solvents. This effect was enhanced for immersion in good solvents, leading to greater resistance variation.
- PP and PCL were tested separately for solvent sorption using ethanol and n-hexane, both showing a low sorption of n-hexane. Ethanol sorption was large for PCL and almost absent for PP. The 50/50 blend composites with 3 wt.% MWNT in the PCL phase presented greater resistance changes for n-hexane, showing larger sensing ability for this solvent compared to PCL composites with 1 and 3 wt.% loadings. The opposite response was observed for immersion in ethanol. This behaviour may be interpreted as follows: since both polymer phases adsorb n-hexane, the nanotube rich phase (PCL) will be spatially more constrained during immersion in n-hexane than in ethanol, resulting in a faster disconnection of the nanotube network.
- The sensing ability of compressed disks and extruded filaments of PCL-3 wt.% MWNT/PP was compared. Samples with similar area-to-volume ratio were tested in poor and good solvents, showing good sensing ability. However, compression-moulded disks presented larger resistivity variation for all solvents tested. This behaviour may be due to differences in the nanotubes arrangement developed in the samples prepared by different techniques.

Acknowledgments

We gratefully acknowledge the financial support from INTELTEX (Intelligent multi-reactive textiles integrating nano-filler based CPC-fibres), a European Integrated Project supported by the Sixth Framework Programme for Research and Technological Development of the European Commission (NMP2-CT-2006-026626).

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Tables

Table 1: Polymer and solvent characteristics (HSP = Hansen solubility parameter δ, [46])

Material	HSP δ ($MPa^{0.5}$)	Molar volume (cm^3/mol)	Boiling point (°C)	Remarks
PCL	17.2-19.2			
PP	19.1-21.2			
n-Hexane	14.9	131.6	69.0	
Toluene	18.2	106.8	110.6	swelling/shrinkage
Chloroform	19.0	80.7	61.2	swelling/shrinkage
Tetrahydrofuran (THF)	19.4	81.7	66.0	swelling/shrinkage
Ethanol	26.6	58.5	78.4	
Methanol	29.7	40.7	64.7	
Water	47.9	18.0	100.0	

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Figures:

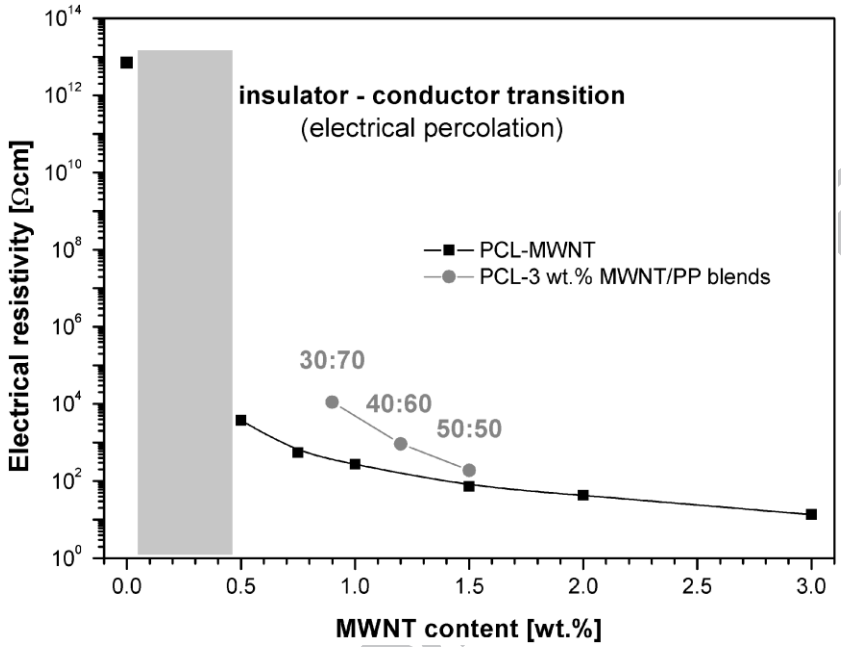

Figure 1: Electrical resistivity of PCL/MWNT composites and PCL-3 wt.% MWNT/PP blend composites

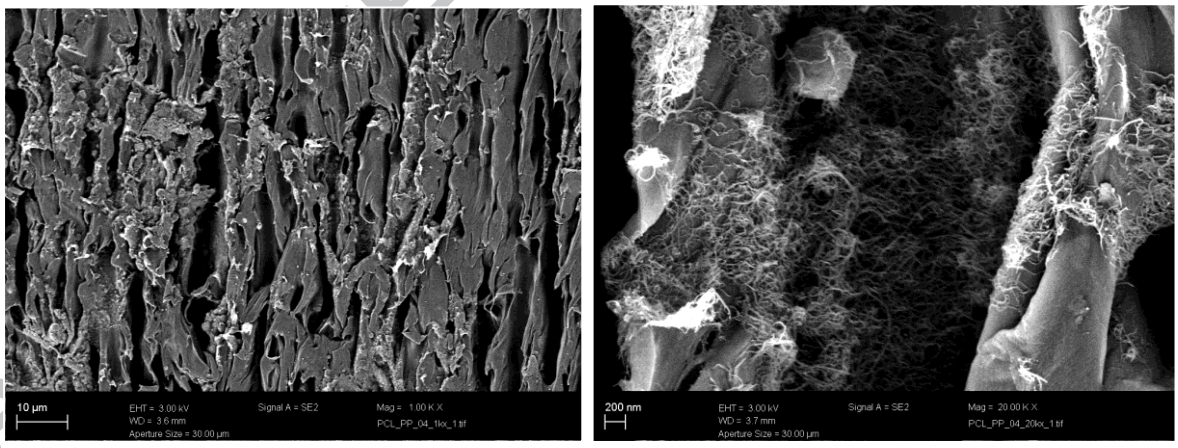

Figure 2: Morphology of PCL-3 wt.% MWNT/PP = 50/50 blends; extruded granules, PCL selectively etched using chloroform (PP phase is remaining) at two different magnifications

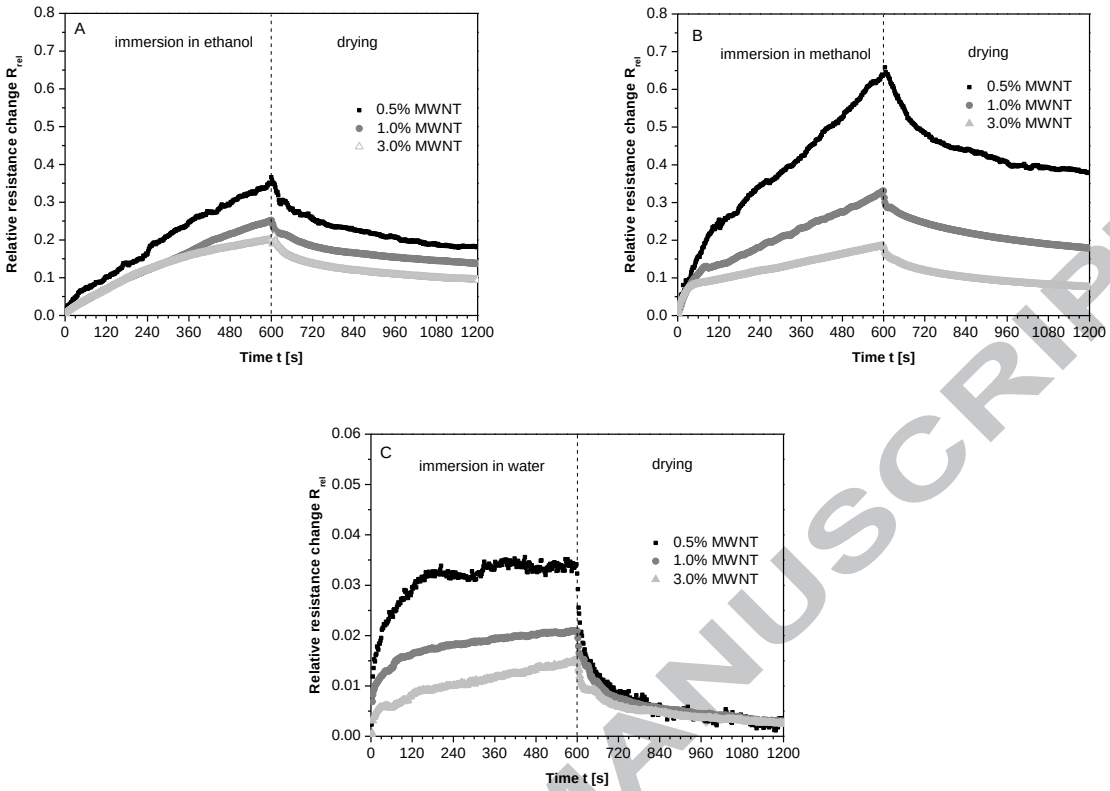

Figure 3: Relative resistance changes of PCL-MWNT disks with different MWNT loadings in poor solvents; A: ethanol, B: methanol, C: water

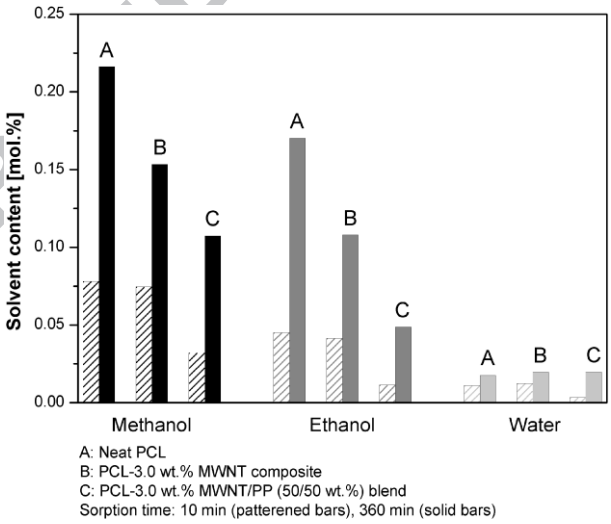

Figure 4: Solvent uptake of neat PCL (A), PCL-3.0 wt.% MWNT (B), and PCL-3 wt.% MWNT/PP = 50/50 blends (C) after immersion in ethanol, methanol, and water for 10 and 360 min

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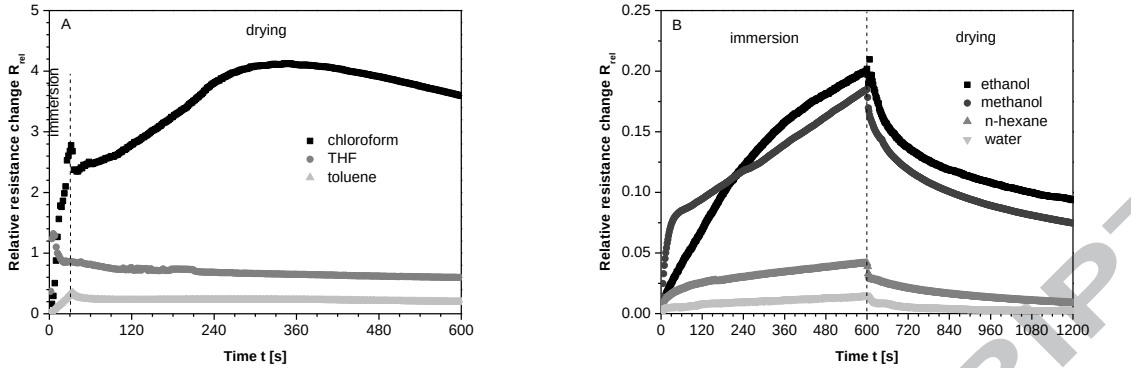

Figure 5: Relative resistance changes of PCL-3 wt.% MWNT on contact with various solvents; A: good solvents, b: poor solvents

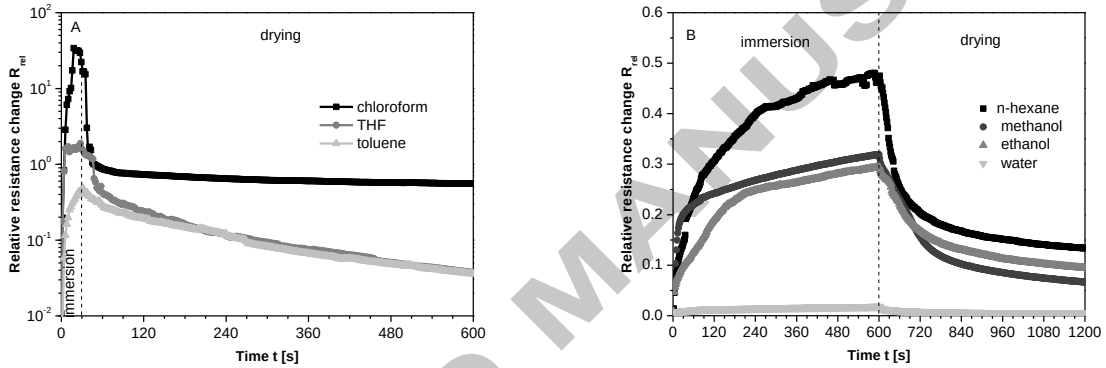

Figure 6: Relative resistance changes of PCL-3 wt.% MWNT/PP = 50/50 blends on contact with various solvents; A: good solvents, B: poor solvents

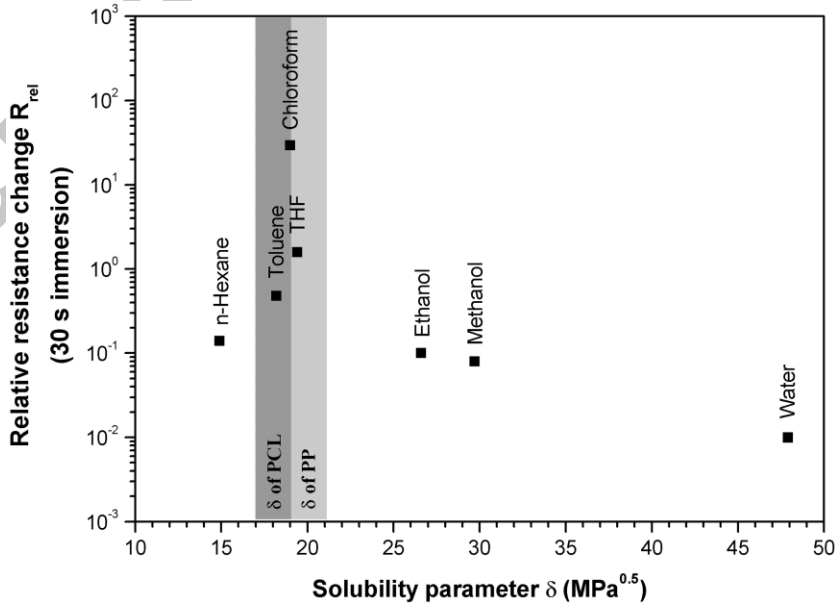

Figure 7: Effect of solvent solubility parameter on relative resistance changes of PCL-3 wt.% MWNT/PP = 50/50 blend composite; the coloured regions represent the HSP region of PCL (17.2-19.2 $MPa^{0.5}$) and PP (19.1-21.2 $MPa^{0.5}$)

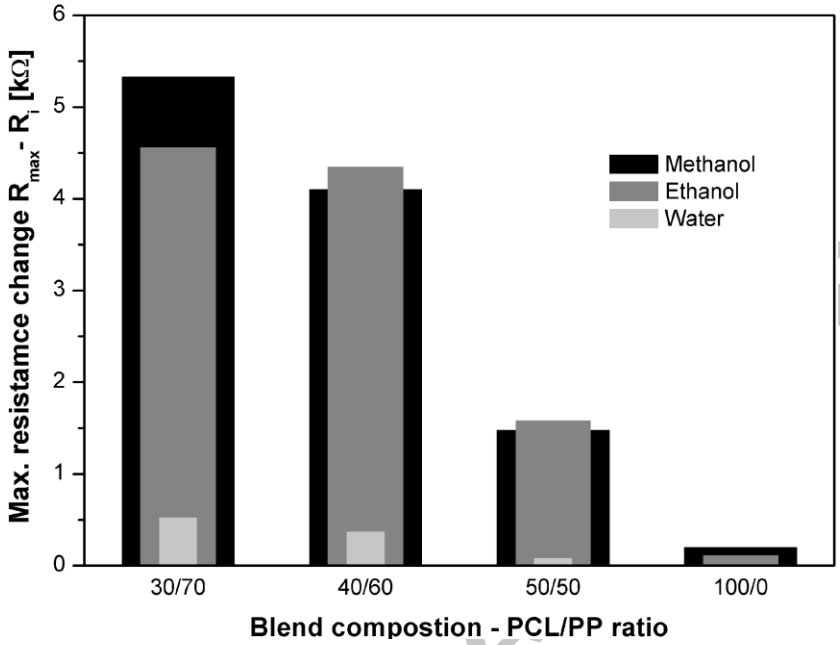

Figure 8: Maximum resistance changes of PCL-3 wt.% MWNT/PP blend composite disks with different blend composition on solvent contact of methanol, ethanol, and water; R_{max}: maximum resistance after 10 min solvent immersion, R_i: initial resistance before immersion

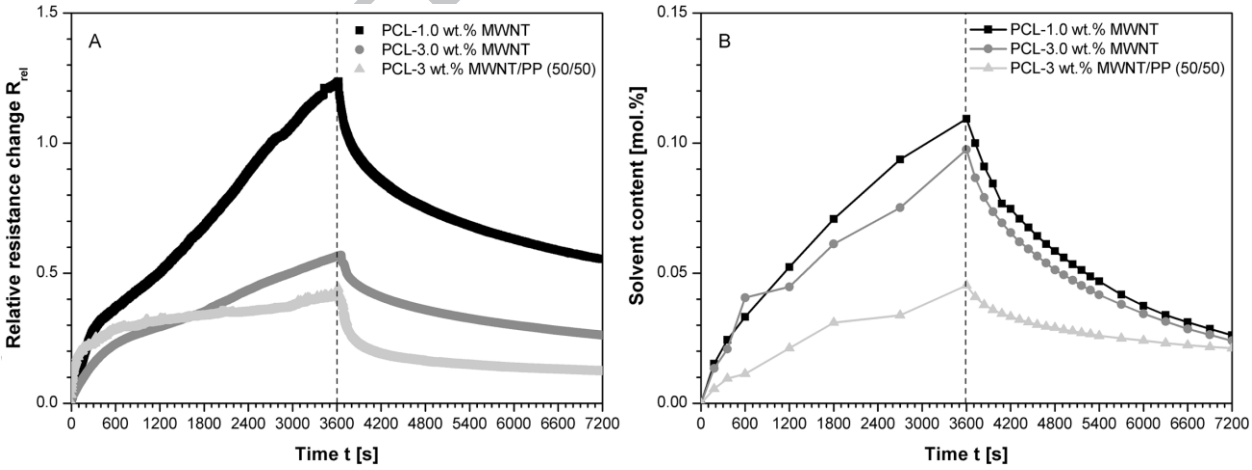

Figure 9: PCL filled with 1.0 and 3.0 wt.% MWNT and PCL-3 wt.% MWNT/PP = 50/50 blend composite in ethanol; A: Relative resistance changes, B: sorption/desorption behaviour

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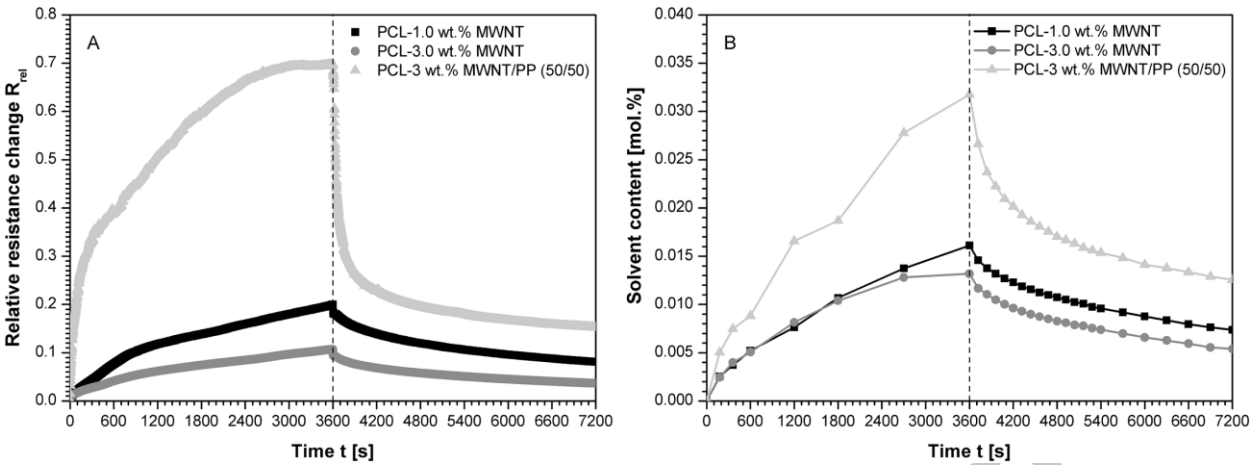

Figure 10: PCL filled with 1.0 and 3.0 wt.% MWNT and PCL-3 wt.% MWNT/PP = 50/50 blend composite in n-hexane; A: Relative resistance changes, B: sorption/desorption behaviour

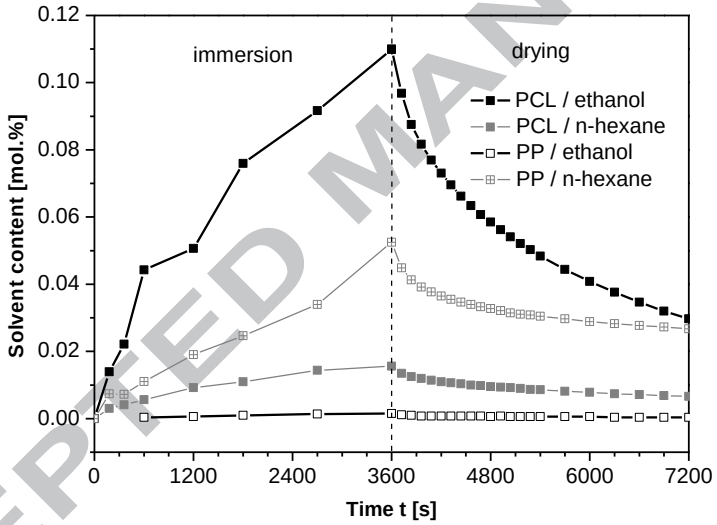

Figure 11: Solvent sorption/desorption behaviours of PCL and PP disks in ethanol and n-hexane

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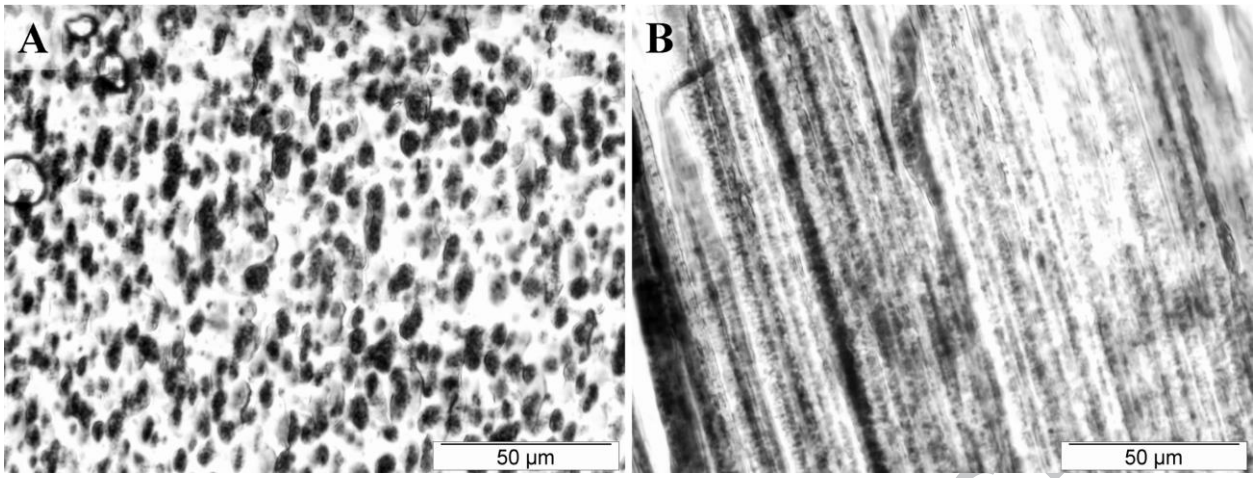

Figure 12: Morphology of a melt-drawn filament of PCL-3 wt.% MWNT/PP = 50/50 blend; A: perpendicular to the filament axis, B: parallel to the filament axis

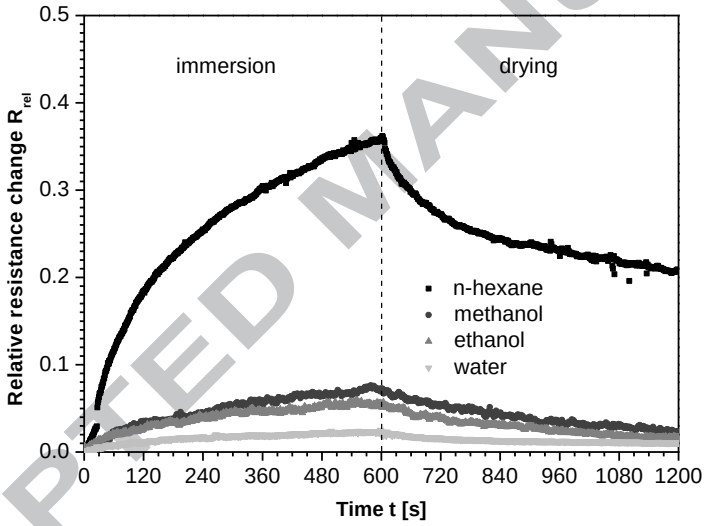

Figure 13: Relative resistance changes of melt-drawn filaments of PCL-3 wt.% MWNT/PP = 50/50 blends on contact with poor solvents