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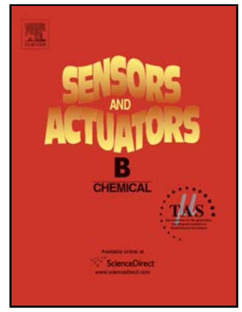

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Liquid sensing of melt-processed poly(lactic acid)/multi-walled carbon nanotube composite films

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Abstract

Liquid sensing properties of poly(lactic acid) (PLA)/multi-walled carbon nanotube (MWNT) composites were studied on the basis of the change of electrical properties on solvent contact. The composites were prepared by melt processing using a twin screw extruder. The MWNT loading differed between 0.5 and 2.0 wt%, and an electrical percolation threshold below 0.5 wt% MWNT content was obtained. TEM observations revealed that the MWNT form a conductive network structure in the PLA matrix, which is the key for liquid sensing. Electrical resistance of the composites was monitored in solvent immersion/drying cycles on samples prepared from thin pressed composite sheets. The resistance reversibly changed upon the cycles with good reproducibility. Lower MWNT loadings resulted in larger resistance changes, indicating that the conductive MWNT network tends to readily disconnect due to the less dense structures as compared to higher loadings. Various solvents (n-hexane, toluene, chloroform, tetrahydrofuran, dichloromethane, ethanol, and water) were successfully detected, showing different degrees of the resistance changes (ca. 4-1.0×10^3 Ω) and the relative resistance changes (ca. 0.003-3.0×10^3).

The solubility parameters of the solvents were found to be good indicators to estimate liquid sensing properties of these PLA/MWNT composites for the poor and good solvents.

Keywords: carbon nanotubes; poly(lactic acid); nanocomposites; melt processing; liquid sensing

1. Introduction

Carbon nanotube (CNT)/polymer composites [1] have been widely reported since the discovery of carbon nanotubes [2]. Due to a unique combination of the electrical, mechanical, optical and thermal properties, their use in polymer nanocomposites is leading to rapidly growing areas of nanotechnology. One of the areas are CNT/polymer composite-based sensors, which were found to sense external stimuli such as biomolecules [3-5], gases [6-17], vapors [6,18,19], taste components [20], mechanical stress [3,6,21], temperature [9,21,22] and pH [23]. Changes of the electrical properties to the stimuli were shown as the sensing behaviors. However, few studies on liquid sensing of CNT/polymer composites have been reported. Even though aqueous solutions were used as an analyte on above-mentioned sensors for taste components and pH, discussions on liquid sensing have not so far been done. A liquid sensor of conductive polymer composite is expected i.e. for applications to detect a solvent leak. Narkis et al. [24] have reported liquid sensing of melt-processed carbon black (CB)/polymer composites. CB chain-like network structures in the polymer matrices, affected by liquid contact, result in changes of the electrical resistance of the composites near the electrical percolation thresholds, leading to the sensing properties. Influences of the melt processing conditions on the sensing properties were discussed. Wall shear rate level in a capillary rheometer had a significant effect on sensitivity of the composite filaments [24]. For CB/single polymer (polyether-type thermoplastic polyurethane) composite, high shear rate resulted in high resistivity and high sensitivity to the exposure to alcohols [24(c)]. Dispersing the conductive particles homogeneously in the polymer matrix and forming a network structure are key issues to obtain good sensing properties. Various CNT/polymer composites have been investigated regarding their CNT dispersion in the polymer matrix and the electrical percolation thresholds. In general, electrical percolation thresholds of melt-processed CNT/polymer composites were reported to be much lower than those of polymer composites containing conventional conductive fillers like CB [25-33]. Unlike CB, very low loading of CNT does not impair mechanical properties of the polymer matrix and furthermore can lead to their improvement. Sensing materials based on conventional conductive fillers-containing polymer composites have been inevitable to make a sacrifice of the mechanical properties and processability due to high loading of the conductive fillers. However, the limitations will be overcome by developing precise CNT conductive network structures in polymer matrices through melt processing. Melt processing of such composites is most compatible with the current processes for industrial applications. Recently we successfully optimised multi-walled carbon nanotube (MWNT) dispersion in poly(lactic acid) (PLA) by melt processing using a twin screw extruder [34].

In this paper, we report liquid sensing properties of these PLA/MWNT composite. The sensing properties were compared among poor and good solvents for PLA according to the solubility parameters. Resistance changes of the composite at different MWNT loading were monitored on the solvent contact. The sensing reversibility and reproducibility were also investigated.

2. Experimental

2.1. Materials, composite, and sample preparation

Biomer® L9000 (PLLA) from Biomer (Germany) is a biodegradable partially crystalline polymer with a glass transition temperature of 55°C and a melting point of app. 170°C. Its chemical structure and solubility parameter are given in Table 1. Due to its susceptibility to water adsorption and degradation, it was dried for at least 18 h at 40°C in a vacuum oven before melt processing. It was melt mixed with Nanocyl®-7000 (Nanocyl S. A. Sambreville, Belgium), which are multi-walled carbon nanotubes produced via the CVD process, having a purity of 90 %. They have a typical diameter of 9.5 nm and an average length of 1.5 µm.

The compounding was performed using a ZE 25 twin screw extruder (Berstorff, Germany) under application of the masterbatch dilution method. As a first step, a masterbatch with 7.5 wt% MWNT content was produced, which then was diluted into 0.5, 0.75, 1.0, 1.5, 2.0 wt% under optimised extrusion conditions [34]. Further properties of these composites, like nanotube macro dispersion index, crystallinity and volume resistivity of pressed plates are discussed in [34]. The influence of MWNT loading on the sensing properties was investigated on a percolation series (0.5-2.0 wt%) which offered very good CNT dispersion in the PLA matrix.

Compression moulding of the materials was performed with a PW 40EH Press (Weber, Germany) under constant pressing conditions to obtain plates with a diameter of 6 cm and thicknesses of 0.1, 0.3, 0.5 mm. The pressing time was set to 3 min at a temperature of 180°C. The pressing procedure was started after a preheating time of 3 min to ensure that the granules were molten with a pressing speed of 6 mm/min. The plates were cooled down for 10 min while kept in the press. For this slowly crystallising material it is expected that no significant changes in crystallinity take place during the pressing procedure [34].

2.2. Material characterization

2.2.1. Electrical resistivity measurements

The electrical resistivity of the PLA/N7000 composites was measured by means of two different measurement devices. Pressed plates with the diameter of 60 mm having electrical resistances $>10^7\ \Omega$ were analysed by means of a Keithley Test Fixture 8009 in combination with a Keithley Multimeter 6517A. Samples with a resistance below $10^7\ \Omega$ were measured 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). For the measurement, strips ($15 \times 4 \times 0.5\ mm^3$) were cut from the pressed plates. This device was combined with a Keithley Electrometer DMM 2000 (measurement range from 10^{-3} to $10^7\ \Omega$).

2.2.2. Morphology investigation

An analytical TEM (Zeiss EM 912, Zeiss, Germany) was employed to investigate the MWNT dispersion within the PLA matrix. The microscope was adjusted with an acceleration voltage of 120 kV. Defocusing and use of a zero loss filter obtained the best contrast between filler and matrix. The thin sections with a thickness of approximately 180 nm were prepared using a Reichert Ultracut S ultramicrotome (Leica, Austria). A diamond knife with a cutting angle of 35° (Diatome, Switzerland) was used. The cutting procedure was carried out at -60°C.

2.2.3. Liquid sensing experiments

The liquid sensing properties of PLA/MWNT composite were examined at different MWNT loading of 0.5, 0.75, 1.0, 1.5, 2.0 wt%. For liquid sensing, U-shaped samples (thickness: 0.1, 0.3, 0.5 mm) were cut from the pressed plates. The electrical resistance change of the samples was monitored using a Keithley 2001 multimeter (measurement range from 10^{-6} to 10^{9} Ω). Resistance values were collected every two seconds. The electrodes were connected to both ends of the U-shaped sample, which were covered by a silver paint, as shown in Fig. 1.

To compare the sensing properties between the composite samples with different MWNT loadings or different thicknesses, the initial resistance at the beginning of the experiment (Ri) and the resistance at time t (R) were taken into account. From both, a relative resistance change (R_{rel}) was calculated according to Equation 1.

$R_{rel} = (R-Ri)/Ri$ (Equation 1)

The samples were immersed in solvent kept at 30°C (in an oil bath) for a given period of time, then taken out and left in air for drying. Solvents used were n-hexane, toluene, chloroform, tetrahydrofuran, dichloromethane, ethanol (purchased from Acros Organics), and distilled water. Their structures, solubility parameters, and boiling points are summarized in Table 1. Different numbers of immersion/drying cycles were performed in order to check reversibility and reproducibility of the sample resistances. Remaining solvent drops on the samples were wiped off at the beginning of drying in case of hexane, ethanol and water. Polymer swelling and shrinkage of the samples were visually seen on solvents having solubility parameters similar to that of PLA (toluene, chloroform, tetrahydrofuran, dichloromethane).

2.2.4. Sorption and desorption experiments

Since the change of electrical resistance of the PLA/MWNT composite is expected to be due to solvent sorption and desorption through the composite, these behaviours were studied on pressed plates of the composite (6 cm in diameter, 0.5 mm in thickness, mass ca. 1.7 g). In case of the sorption experiments, the plates were immersed in ethanol kept at 30°C for a given period of time before it was taken out to weigh the solvent uptake. Different plates were used for different sorption times. Remaining solvent drops on the plates were wiped off. The weight was measured within 20-30 sec after removing the plates from the solvent.

For desorption experiments, the pressed plates were first immersed in the solvent for 60 min, and then taken out from the solvent for the drying in air for 60 min. The weight loss of desorbed solvent was started to monitor after wiping off all solvent left on the plates at the beginning of the drying. The solvent content *S* of the plates at time *t* was calculated by taking into account the weight at time t (m_t) and the initial weight (m_i) (Equation 2).

$$S = \frac{m_t - m_i}{m_t} * 100\% \qquad \text{(Equation 2)}$$

For these sorption and desorption experiments, the plates were dried under vacuum for at least 18 h at 40°C prior to all the immersion in the solvent.

2.2.5. Dissolution experiments

Pressed plates of PLA/MWNT (6 cm in diameter, 0.5 mm in thickness, mass ca. 1.7 g) were immersed in chloroform kept at 30^{o}C for 30 sec. The samples were dried under vacuum at 40^{o}C until the constant weight values.

3. Results and discussion

3.1. Conductive network state in the composites

The PLA/MWNT composites used were obtained after the optimisation of extrusion conditions which was performed with the aim to achieve a very good state of CNT dispersion within the polymer matrix [34]. The liquid sensing properties were examined at different MWNT loadings of 0.5, 0.75, 1.0, 1.5, 2.0 wt%. The 0.5 wt% sample is already percolated, but near the electrical percolation threshold, and those samples with higher MWNT amounts are electrically conductive with resistivity values below 10^2 Ωcm (Fig. 2). These samples show a very good MWNT dispersion within the PLA matrix. No MWNT agglomerates in the micron scale were visible using light microscopy. Also TEM investigations have shown that the MWNT are well dispersed. Furthermore, the TEM images obtained on thin sections suggest the existence of a three-dimensional MWNT network-like structure within the PLA matrix at all MWNT loadings, as it is shown exemplarily in Fig. 3 for 0.75 wt%. The image shows next to single tubes MWNT small clusters with a typical diameter of about 500 nm. The individual nanotubes are interconnected to form the clusters. These clusters seem to be connected, which leads to a conductive network, spreading over the whole bulk material. Denser network structures were observed at the higher MWNT loading. These PLA/MWNT composites are expected to work as a liquid sensor based on the change of the MWNT network structure during solvent contact. Some parameters of PLA and the solvents used for liquid sensing experiments are listed in Table 1.

3.2. Sensing behaviour on contact towards poor solvent (ethanol)

Firstly, samples with 0.75 wt% MWNT loading and 0.5 mm thickness were investigated against ethanol as an example for a poor solvent over 3600 sec immersion and 3600 sec drying in air (Fig. 4). As shown in Table 1, the solubility parameter (δ) of ethanol is 26.6 $MPa^{0.5}$, whereas δ values of poly(lactic acid) have been reported to be 19.2-21.0±0.3 $MPa^{0.5}$ for PDLLA and 19.0-20.5 $MPa^{0.5}$ for PLLA [35]. Two materials tend to be miscible if their solubility parameters are close to each other. Ethanol and PLA possess different δ values, resulting in a poor solubility of PLA for ethanol.

The MWNT loading of 0.75 wt% was selected for most of the investigations since it shows a good combination of large resistance changes and relatively low noise of resistance values (as discussed later). The electrical resistance change of the U-shaped PLA/MWNT sample on the solvent contact is plotted in Fig. 4 together with the solvent sorption and desorption behaviours of the plates. During the immersion, a gradual increase of the resistance was observed with an increase of absorbed solvent content. The absorbed solvent content was ~1.0 wt%. Immediately after the start of drying, a sharp drop in the resistance was seen, showing good reversibility of the resistance. On the other hand, the content of sorbed solvent content slightly decreased during the drying and ~0.8 wt% of solvent was left. These results indicate that a very small amount of solvent ~0.2 wt% leads to the resistance drop to which the surface structure of PLA/MWNT strip is primarily related. It was found that the PLA/MWNT composite possesses good reversibility of the resistance on ethanol contact. However, even one hour after the drying, the resistance was about 20 kΩ higher than the initial value before the testing. This may be assigned to a low degree of solvent-induced crystallisation [35(b)] as discussed in more detail in [36]. The U-shaped sample and the plates used for sorption/desorption were vacuum-dried at 40°C for three days, which gave a close resistance value to the initial one and ~0.3 wt% larger weight than the initial one. This indicates that solvent molecules were left deep in the PLA/MWNT samples one hour after the drying in air, and affected the slightly higher resistance.

Based on these data, resistance changes of U-shaped PLA/MWNT samples with 0.5 mm thickness were investigated in ethanol at different loading. Ten minutes immersion and ten minutes drying were applied. Good responses and good reversibility of the resistance were obtained at all loadings. Gradual increases of resistance upon immersion and sharp drops upon drying were observed like it was shown for PLA/0.75 wt% MWNT during 60 min immersion and 60 min drying (see Fig. 4). MWNT loading had a considerable influence on the resistance changes as shown in Fig. 5. After 10 min of drying, the resistance values nearly came back to the initial ones. In addition, the relative resistance change R_{rel} is shown to make a better comparison at different loadings. As the loading decreases, larger R_{rel} values were observed, indicating that conductive MWNT networks in PLA tend to readily disconnect at lower loading because of the less dense nanotube network structure. In addition, the noise level of resistance decreased with an increase of the nanotube content indicating more stable signals. In order to have both of high and stable signals, we selected the concentration of 0.75 wt% as a reference for further investigations. Subsequently, the reproducibility of resistance changes of PLA/MWNT composites on ethanol contact was examined with the U-shaped sample with 0.5 mm thickness and 0.75 wt% MWNT loading. Five cycles of two min immersion/eight min drying in air were applied (Fig. 6). The results indicate good responses and good reversibility of the resistance in each cycle. The slopes of the resistance curves in initial 1 min immersion of each cycle were estimated to be 0.35, 0.54, 0.72, 0.61, and 0.69 (kΩ/sec) for first to fifth cycles. The values of the slope increased gradually as the number of cycle multiplies. The values of resistance at the beginning of each cycle were 37.3, 41.5, 42.2, 40.8, and 42.6 (kΩ) for first to fifth cycles. Constant values of approximately 41 kΩ were recorded starting from the second cycle, which are slightly higher than that of the first cycle. As discussed in the long time immersion (3600 sec) with ethanol, a small amount of solvent can be left in the sample, resulting in the slightly higher resistances after the first drying in air. These results revealed that the PLA/MWNT composite exhibits relatively good reproducibility of the resistance curve on ethanol contact. An influence of sample thickness on resistance change in ethanol was also examined using PLA/MWNT samples with 0.75 wt% loading. Ten minutes immersion and ten minutes drying in air were carried out. The U-shaped samples with different thickness (0.1, 0.3, 0.5 mm) showed somewhat different changes of the relative resistance change R_{rel} (Fig. 7). The thinner sample resulted in a sharper response and a faster recovery of the resistance. This result suggests that solvent molecules absorb and desorb from the surface of PLA/MWNT composite and the overall resistance changes are affected by the ratio of the surface area to the volume.

3.3. Sensing behaviour on contact towards good solvent (chloroform)

As a second solvent to be investigated, chloroform with a solubility parameter δ of 19.0 $MPa^{0.5}$ (Table 1) was chosen as a good solvent for PLA to compare with the liquid sensing property of PLA/MWNT composites in ethanol. The resistance changes of U-shaped PLA/MWNT samples (0.5 mm thick) were investigated in chloroform at different loadings (Fig. 8). Unlike the liquid sensing of ethanol, a short immersion time of 30 seconds was applied because of chloroform's excellent solubility and the resultant too fast response. After the immersion, the U-shaped samples were dried in air for 9 min and 30 sec. Sharp responses were obtained at all loadings. The MWNT loading was significantly influential on the resistance change. Larger changes in the resistance were seen at lower loading as well as in the results of liquid sensing in ethanol. At the lowest loading of 0.5 wt%, the resistance reached ~10^8 Ω starting from the initial value R_i of ca. 1.4×10^5 Ω. The degree of the resistance change (three orders of magnitude) was much larger than that in ethanol at the same loading of 0.5 wt%. The relative resistance change R_{rel} provided a good comparison of the liquid sensing ability at different loading. In these samples, polymer swelling and shrinkage was observed during the sensing tests. To observe the swelling state of the inside, U-shaped samples of the PLA/0.75 wt% MWNT composites with 0.5 mm thicknesses were immersed in a good solvent, chloroform for 10, 30, 60, 120, 180, and 240 sec. We cut the samples and looked visually at the inside immediately after taking out from the solvent. In addition, the sample was stretched using tweezers to see the overall "hardness". After 10 sec immersion, the sample was visibly swollen and softened. The surface became sticky, but, the inside was stiff. After 30 sec of immersion, the solvent molecules penetrated deeper into the inside; however, the innermost was still stiff. The whole of the sample became jelly with a further increase of the immersion time. At 240 sec, the sample was easily broken when stretching by tweezers. Thus, the solvent content appeared to be higher in the vicinity of the surface. This indicates that the swelling of the polymer was not homogeneous over the total thickness but starts from the surface and continues over time to the inner part. The immersed parts of all the U-shaped samples turned white or gray, which suggested a weight loss of the samples which, however, could not be proven in other tests. Dissolution tests of PLA/MWNT plates (0.75 wt% loading, 0.5 mm thick) were done for 30 sec immersion in chloroform. After taking out the sample it was vacuum-dried at 40°C to a constant weight value, resulting in about 10 wt% higher weight than that of the original sample. This clearly indicates that some amount of chloroform was trapped in the plate. To remove this part of solvent left, vacuum drying at higher temperature of 150°C was carried out, which resulted in hardened plates with the original weight. However, drying at this temperature is always accompanied by crystallisation; thus, the state of the sample is not comparable anymore to that after solvent immersion. The trapped solvent in the plate is supported by the data of the corresponding sample on contact of ethanol (see Fig. 4).

The values of the resistance at high loading somewhat reversed with drying even after the polymer swelling during the immersion, whereas those with 0.75 wt% and 1.0 wt% MWNT loading did not show reversibility. All the U-shaped samples vacuum-dried at 40°C for three days showed relatively high resistances compared with the initial values, which implies that the solvent molecules are left deep in the samples.

These results indicate that MWNT conductive networks can be partly reconnected in the process of polymer shrinkage accompanied by solvent desorption. However, they do not reach the original network state due to remaining solvent molecules which increase the intertube contact resistance. This non-reversibility is especially pronounced at low loadings where the destructed networks remained even after drying. Due to penetration of the larger amount of chloroform solvent into PLA matrix than that in ethanol, followed by polymer swelling, the resistance changed to a large extent on solvent contact of chloroform. It can be suggested that the internal structure of the sample is related to the large resistance changes as well as the surface structure.

3.4. Sensing behaviour on contact towards various solvents

Liquid sensing tests in various solvents were carried out with U-shaped PLA/MWNT samples containing 0.75 wt% loading (Fig. 9). A significant increase of the resistance was observed in good solvents for PLA (toluene, chloroform, THF, dichloromethane) having δ of 18.2-20.3 $MPa^{0.5}$ close to that of PLA (see Table 1) and the resistance somewhat decreased with drying. For the sensing on n-hexane having a smaller δ of 14.9 $MPa^{0.5}$ than PLA (Table 1), a good response and reversibility of the resistance was obtained in spite of only a slight change of resistance. The resistance change was smaller than that in ethanol. On the other hand, after exposure to water with a large δ of 47.9 $MPa^{0.5}$, much higher than PLA (Table 1), no change of resistance of the PLA/MWNT sample was detected at the loading of 0.75 wt%. Liquid sensing on PLA/MWNT samples with 2.0 wt% loading was performed using five cycles of two minutes immersion and eight minutes drying in air. The initial resistance of 1.224 kΩ was much smaller than that at the low loading of 0.75 wt%. It was observed that the signal to noise ratio at higher loading is higher as compared to that at the lower loading. A clear change of the resistance was detected as shown in Fig. 10, even though the change is very small. The most probable reason for no detection of water at low loading of 0.75 wt% is that the change of the resistance was overlapped with higher noise level at lower loading. Therefore, the PLA/MWNT composite can also sense water, which is a poor solvent for PLA, however, only at higher MWNT loadings. Regarding water sensing, PLA/MWNT composite with higher nanotube loadings would be promising from the viewpoint of detectability.

3.5. Comparison of sensing behavior towards different solvents

These results on various solvents confirmed that solubility parameters have a correlation with the liquid sensing of PLA/MWNT composite. Solvents having δ closer to that of PLA were detected with larger and faster resistance increases. In this context it has to be mentioned again that the solubility parameter range of PLLA compared here resulted from an experimental study investigating the degree of swelling in different solvents [35]. On the other hand, solvents with smaller or larger δ than that of PLA were also detected, resulting in smaller and slower resistance increases. For all the composite samples in this study, the ranges of the resistance changes and the relative resistance changes R_{rel} were ca. 4-1.0×10^3 Ω and ca. 0.003-3.0×10^3, respectively. Resistance increases of PLA/0.75 wt% MWNT composite after 30 seconds solvent immersion were plotted against δ of various solvents in Fig. 11. Good solvents with δ close to the range of PLA like chloroform, tetrahydrofuran, and dichloromethane resulted in large resistance increases, while poor solvents with significantly smaller or larger δ than the range for PLA like n-hexane and ethanol yielded smaller resistance increases. Toluene having a moderate distance in solubility parameter to PLA resulted in medium changes. By these resistance change kinetics on solvent contact, various solvents may be distinguishable. According to our investigations it may be suggested that the solubility parameter of PLLA is close to 20.5 MPa$^{0.5}$ since the solvent having this solubility parameter (dichloromethane) shows the highest impact on resistance and, thus, on polymer swelling assumed to be responsible for changes in the electrical network.

4 Summary

Liquid sensing properties of melt-processed PLA/MWNT composites were investigated by means of the electrical resistance change on solvent contact. Thin pressed composite sheets containing 0.5-2.0 wt% MWNT were used for the sensing. Good responses, good reversibility and reproducibility of the resistance were obtained depending on the kind of solvent as well as immersion and drying time. The MWNT loading had a significant influence on the resistance change. Lower loadings resulted in larger changes but also higher signal noises. For all the composite samples on contact of various solvents, the resistance changes and the relative resistance changes R_{rel} ranged ca. 4-1.0×10^3 Ω and ca. 0.003-3.0×10^3, respectively. MWNT conductive network structures in PLA matrix, shown by TEM observation, are important for liquid sensing. The solubility parameter is a good indicator to estimate the sensing property of the composite for the poor and good solvents. PLA/MWNT composite can sense poor solvents for PLA like ethanol, n-hexane, and water as well as good solvents like toluene, chloroform, tetrahydrofuran, and dichloromethane. In this comparison, good solvents having δ close to that of PLA result in larger and faster resistance increases, whereas poor solvents with more different δ values lead to smaller and slower resistance increases. Thus, it may be possible to distinguish from the resistance change kinetics on the immersing solvent. Due to the polymer characteristic, good solvents applied over a long time may hydrolyse or dissolve the polymer matrix which restricts the sensor materials to short time or one-use applications. Nevertheless, these melt-processed PLA/MWNT composites are promising candidates for applications like leakage detection of various solvents.

However, in order to understand all the effects and the mechanism of liquid sensing of such polymer-nanotube composites more investigations are needed. Additional investigations on PLA-MWNT composites are presented in [36].

In summary we can conclude that thin films of composite materials based on thermoplastic matrices and multi-walled carbon nanotubes prepared by melt mixing are able to be adapted in sensors for liquid sensing.

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References

[1] M. Moniruzzaman, K. I. Winey, Polymer nanocomposites containing carbon nanotubes, Macromolecules 39 (2006) 5194-5205.

[2] S. Iijima, Helical microtubules of graphitic carbon, Nature 354 (1991) 56-58.

[3] I. Kang, Y. Y. Heung, J. H. Kim, J. W. Lee, R. Gollapudi, S. Subramaniam, S. Narasimhadevara, D. Hurd, G. R. Kirikera, V. Shanov, M. J. Schulz, D. Shi, J. Boerio, S. Mall, M. Ruggles-Wren, Introduction to carbon nanotube and nanofiber smart materials, Compos. Part B: Eng. 37 (2006) 382-394.

[4] A. Merkoçi, M. Pumera, X. Llopis, B. Pérez, M. del Valle, S. Alegret, New materials for electrochemical sensing VI: Carbon nanotubes, Trends Anal. Chem. 24 (2005) 826-838.

[5] M. Pumera, S. Sánchez, I. Ichinose, J. Tang, Electrochemical nanobiosensors, Sens. and Actuators B 123 (2007) 1195-1205.

[6] C. Li, E. T. Thostenson, T.-W. Chou, Sensors and actuators based on carbon nanotubes and their composites: A review, Compos. Sci. Technol. 68 (2008) 1227-1249.

[7] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. Dai, Nanotube molecular wires as chemical sensors, Science 287 (2000) 622-625.

[8] P. Qi, O. Vermesh, M. Grecu, A. Javey, Q. Wang, H. Dai, S. Peng, K. J. Cho, Toward large arrays of multiplex functionalised carbon nanotube sensors for highly sensitive and selective molecular detection, Nano Lett. 3 (2003) 347-351.

[9] L. Valentini, I. Armentano, J. M. Kenny, C. Cantalini, L. Lozzi, S. Santucci, Sensors for sub-ppm NO_2 gas detection based on carbon nanotube thin films, Appl. Phys. Lett. 82 (6) (2003) 961-963.

[10] J. K. Abraham, B. Philip, A. Witchurch, V. K. Varadan, C. C. Reddy, A compact wireless gas sensor using a carbon nanotube/PMMA thin film chemiresistor, Smart Mater. Struct. 13 (2004) 1045-1049.

[11] K. H. An, S. Y. Jeong, H. R. Hwang, Y. H. Lee, Enhanced sensitivity of a gas sensor incorporating single-walled carbon nanotube-polypyrrole nanocomposites, Adv. Mater. 16 (2004) 1005-1009.

[12] Y. Lu, C. Partridge, M. Meyyappan, J. Li, A carbon nanotube sensor array for sensitive gas discrimination using principal component analysis, J. Electroanal. Chem. 593 (2006) 105-110.

[13] Y. Wanna, N. Srisukhumbowornchai, A. Tuantranont, A. Wisitsoraat, N. Thavarungkul, P. Singjai, The effect of carbon nanotube dispersion on CO gas sensing characteristics of polyaniline gas sensor, J. Nanosci. Nanotech. 6 (2006) 3893-3896.

[14] H. Yoon, J. Xie, J. K. Abraham, V. K. Varadan, P. B. Ruffin, Passive wireless sensors using electrical transition of carbon nanotube junctions in polymer matrix, Smart Mater. Struct. 15 (2006) 14-20.

[15] T. Zhang, M. B. Nix, B.-Y. Yoo, M. A. Deshusses, N. V. Myung, Electrochemically functionalised single-walled carbon nanotube gas sensor, Electroanalysis 18 (2006) 1153-1158.

[16] K. Cattanach, R. D. Kulkarni, M. Kozlov, S. K. Manohar, Flexible carbon nanotube sensors for nerve agent simulants, Nanotechnology 17 (2006) 4123-4128.

[17] H.-L. Hsu, J.-M.-Jehng, Y. Sung, L.-C. Wang, S.-R. Yang, The synthesis, characterization of oxidized multi-walled carbon nanotubes, and application to surface acoustic wave quartz crystal gas sensor, Mater. Chem. Phys. 109 (2008) 148-155.

[18] V. Bavastrello, E. Stura, S. Carrara, V. Erokhin, C. Nicolini, Poly(2,5-dimethylaniline)-MWNTs nanocomposite: a new material for conductometric acid vapours sensor, Sens. and Actuators B 98 (2004) 247-253.

[19] L. Valentini, V. Bavastrello, E. Stura, I. Armentano, C. Nicolini, J. M. Kenny, Sensors for inorganic vapor detection based on carbon nanotubes and poly(*o*-anisidine) nanocomposite material, Chem. Phys. Lett. 383 (2004) 617-622.

[20] T. Hirata, K. Takagi, M. Akiya, Development of a taste sensor based on a carbon nanotube-polymer composite material, Jap. J. Appl. Phys. 46 (2007) 314-316.

[21] J. R. Wood, Q. Zhao, M. D. Frogley, E. R. Meurs, A. D. Prins, T. Peijs, D. J. Dunstan, H. D. Wagner, Carbon nanotubes: From molecular to macroscopic sensors, Phys. Rev. B 62 (2000), 7571-7575.

[22] N. Koratkar, A. Modi, E. Lass, P. J. Ajayan, Temperature effects on resistance of aligned multiwalled carbon nanotube films, J. Nanosci. Nanotech. 4 (2004) 744-748.

[23] N. Ferrer-Anglada, M. Kaempgen, S. Roth, Transparent and flexible carbon nanotube/polypyrrole and carbon nanotube/polyaniline pH sensors, Physica Status Solidi 243 (2006) 3519-3523.

[24] (a) M. Narkis, S. Srivastava, R. Tchoudakov, O. Breuer, Sensors for liquid based on conductive immiscible polymer blends, Synth. Met. 113 (2000) 29-34. (b) S. Srivastava, R. Tchoudakov, M. Narkis, A preliminary investigation of conductive immiscible polymer blends as

sensor materials, Polym. Eng. Sci. 40 (2000) 1522-1528. (c) E. Segal, R. Tchoudakov, M. Narkis, Thermoplastic polyurethane-carbon black compounds: structure, electrical conductivity and sensing of liquids, Polym. Eng. Sci. 42 (2002) 2430-2439. (d) E. Segal, R. Tchoudakov, M. Narkis, A. Siegmann, Sensing of liquids by electrically conductive immiscible polypropylene/thermoplastic polyurethane blends containing carbon black, J. Polym. Sci. Part B: Polym. Phys. 41 (2003) 1428-1440. (e) E. Segal, R. Tchoudakov, I. Mironi-Harpaz, M. Narkis, A. Siegmann, Chemical sensing materials based on electrically-conductive immiscible polymer blends, Polym. Int. 54 (2005) 1065-1075.

[25] (a) J. Sandler, M. S. P. Shaffer, T. Prasse, W. Bauhofer, K. Schulte, A. H. Windle, Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties, Polymer 40 (1999) 5967-5971. (b) J. K. W. Sandler, J. E. Kirk, I. A. Kinloch, M. S. P. Shaffer, A. H. Windle, Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites, Polymer 44 (2003) 5893-5899.

[26] R. Andrews, D. Jacques, M. Minot, T. Rantell, Fabrication of carbon multiwall nanotube/polymer composites by shear mixing, Macromol. Mater. Eng. 287 (2002) 395-403.

[27] (a) P. Pötschke, T. D. Fornes, D. R. Paul, Rheological behavior of multiwalled carbon nanotube/polycarbonate composites, Polymer 43 (2002) 3247-3255. (b) P. Pötschke, A. R. Bhattacharyya, A. Janke, H. Goering, Melt mixing of polycarbonate/multi-wall carbon nanotube composites, Compos. Interf. 10 (2003) 389-404. (c) P. Pötschke, A. R. Bhattacharyya, A. Janke, Morphology and electrical resistivity of melt mixed blends of polyethylene and carbon nanotube filled polycarbonate, Polymer 44 (2003) 8061-8069. (d) P. Pötschke, A. R. Bhattacharyya, I. Alig, S. M. Dudkin, A. Leonhardt, C. Täschner, M. Ritschel, S. Roth, B. Hornbostel, J. Cech, Dispersion of carbon nanotubes into thermoplastic polymers using melt mixing, AIP conference proceedings 723, Electronic Properties of Synthetic Nanostructures (2004) 478-482. (e) P.

Pötschke, A. R. Bhattacharyya, A. Janke, Carbon nanotube-filled polycarbonate composites produced by melt mixing and their use in blends with polyethylene, Carbon 42 (2004) 965-969. (f) P. Pötschke, A. R. Bhattacharyya, A. Janke, S. Pegel, A. Leonhardt, C. Täschner, M. Ritschel, S. Roth, B. Hornbostel, J. Cech, Melt mixing as method to disperse carbon nanotubes into thermoplastic polymers, Fullerenes, Nanotubes, and Carbon Nanostructures 13 (2005) 211-224. (g) B. Lin, U. Sundararaj, P. Pötschke, Melt mixing of polycarbonate with multi-walled carbon nanotubes in miniature mixers, Macromol. Mater. Eng. 291 (2006) 227-238.

[28] (a) B. Hornbostel, M. Dubosc, P. Pötschke, S. Roth, Investigations on polycarbonate-nanotube composites, AIP conference proceedings 723, Electronic Properties of Synthetic Nanostructures (2004) 473-477. (b) B. Hornbostel, P. Pötschke, J. Kotz, S. Roth, Single-walled carbon nanotubes/polycarbonate composites: basic electrical and mechanical properties, Phys. Stat. Sol. B 243 (2006) 3445-3451.

[29] G. B. Blanchet, C. R. Fincher, F. Gao, Polyaniline nanotube composites: A high-resolution printable conductor, Appl. Phys. Lett. 82 (2003) 1290-1292.

[30] F. Du, R. C. Scogna, W. Zhou, S. Brand, J. E. Fischer, K. I. Winey, Nanotube networks in polymer nanocomposites: Rheology and electrical conductivity, Macromolecules 37 (2004) 9048-9055.

[31] O. Regev, P. N. B. Elkati, J. Loos, C. E. Koning, Preparation of conductive nanotube-polymer composites using latex technology, Adv. Mater. 16 (2004) 248-251.

[32] R. Ramasubramaniam, J. Chen, H. Liu, Homogeneous carbon nanotube/polymer composites for electrical applications, Appl. Phys. Lett. 83 (2003) 2928-2930.

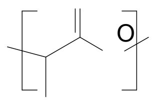
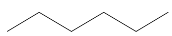
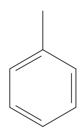
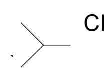
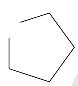
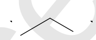
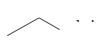
[33] O. Meincke, D. Kaempfer, H. Weickmann, C. Friedrich, M. Vathauer, H. Warth, Mechanical properties and electrical conductivity of carbon-nanotube filled polyamide-6 and its blends with acrylonitrile/butadiene/styrene, Polymer 45 (2004) 739-748.

[34] T. Villmow, P. Pötschke, S. Pegel, L. Häußler, B. Kretzschmar, Influence of twin screw extrusion conditions on the dispersion of multi-walled carbon nanotubes in a poly(lactic acid) matrix, accepted, Polymer, 2008.

[35] (a) U. Siemann, The solubility parameter of poly($_{DL}$-lactic acid), Eur. Polym. J. 28 (1992) 293-297. (b) H. Tsuji, K. J. Sumida, Poly($_{L}$-lactide): V. Effects of storage in swelling solvents on physical properties and structure of poly($_{L}$-lactide), J. Appl. Polym. Sci. 79 (2001) 1582-1589.

[36] K. Kobashi, T. Villmow, T. Andres, L. Häußler, P. Pötschke, Investigation of liquid sensing mechanism of poly (lactic acid) / multi-walled carbon nanotube composite films, submitted to Journal of Nanomaterials.

Table 1 Polymer and solvent characteristics

Material	Chemical structure	Solubility parameter δ ($MPa^{0.5}$)	Boiling point (°C)	Remarks
Poly(lactic acid)		19.2-21.0 ± 0.3 (PDLLA)[a] 19.0-20.5 (PLLA)[a]	-	-
n-Hexane		14.9	69.0	-
Toluene		18.2	110.6	Polymer swelling/shrinkage
Chloroform		19.0	61.2	Polymer swelling/shrinkage
Tetrahydrofuran		19.4	66.0	Polymer swelling/shrinkage
Dichloromethane		20.3	39.8	Polymer swelling/shrinkage
Ethanol		26.6	78.4	-
Water		47.9	100.0	-

a: Cited from ref. [35].

Biographies

Kazufumi Kobashi received the BS and MS degrees in polymer chemistry, and the Ph.D. in engineering from Okayama University, Japan in 1999, 2001, and 2004, respectively. He is currently a scientific coworker at the Leibniz Institute of Polymer Research Dresden, Germany. His research interests include polymer nanocomposites, organic sensors, and polymer whiskers.

Tobias Villmow received the academic degree Graduate engineer (University of Applied Sciences, Senftenberg, Germany) in Mechanical Engineering in 2006. Since 2007 he is working as scientific coworker at the Leibniz Institute of Polymer Research Dresden in Germany. His fields of work are polymeric nanocomposites based on carbon nanotubes, whereas the research is focused on the investigation of processing- property- relationships of melt mixed composites.

Timo Andres received the academic degree Graduate engineer (University of Applied Sciences, Augsburg, Germany) in Mechatronics and the academic degree Master of Engineering (University of Ulster, Northern Ireland) in 2007. Since 2007 he is working as scientific coworker at the Leibniz Institute of Polymer Research Dresden in Germany. His fields of work are polymeric nanocomposites based on carbon nanotubes, whereas the research is focused on the investigation of sensor applications with respect to liquid sensing.

Petra Pötschke received her diploma and PhD in mechanical engineering from the Dresden University of Technology. Since 1988 she has been working at the Leibniz Institute of Polymer Research Dresden, Germany. 1999/2000 she worked with a grant of the Max-Kade-Foundation at the University of Texas at Austin, USA. She currently heads the working group of Composites and Blends with Carbon Nanoparticles.

Captions of figures

Fig. 1. U-shaped PLA/MWNT sample as used for liquid sensing.

Fig. 2. Electrical resistivity of PLA/MWNT composites depending on the MWNT loading.

Fig. 3. TEM images of PLA/MWNT composite prepared at the MWNT loading of 0.75 wt%

Fig. 4. Changes of the resistance and solvent content of PLA/MWNT composite (0.75 wt% loading, 0.5 mm thick) on contact of ethanol in 3600 sec solvent immersion/3600 sec drying process.

Fig. 5. Resistance changes of PLA/MWNT composites (0.5 mm thick) in ethanol, depending on MWNT loading.

Fig. 6. Resistance change of PLA/MWNT composite (0.75 wt% loading, 0.5 mm thick) in ethanol.

Fig. 7. Resistance changes of PLA/MWNT composites (0.75 wt% loading) in ethanol, depending on the sample thickness.

Fig. 8. Resistance changes of PLA/MWNT composites (0.5 mm thick) in chloroform, depending on MWNT loading.

Fig. 9. Resistance changes of PLA/MWNT composite (0.75 wt% loading, 0.5 mm thick) in various solvents. The values of the solubility parameter δ in $MPa^{0.5}$ are given in parentheses.

Fig. 10. Resistance change of PLA/MWNT composite (2.0 wt% loading, 0.5 mm thick) in water.

Fig. 11. Resistance increases of PLA/MWNT composite (0.75 wt% loading, 0.5 mm thick) on 30 seconds immersion in various solvents having different solubility parameters. R_{30s}: Resistance values after 30 seconds solvent immersion, R_i: Initial resistance values before the immersion. A dotted region is shown for the solubility parameter of PLLA (19.0-20.5 $MPa^{0.5}$) as reported from literature [35].

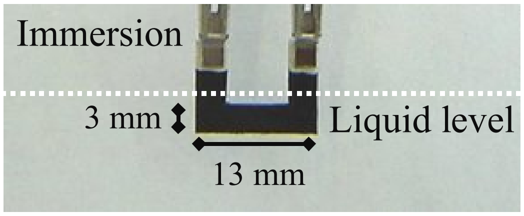


Fig. 1. U-shaped PLA/MWNT sample as used for liquid sensing.

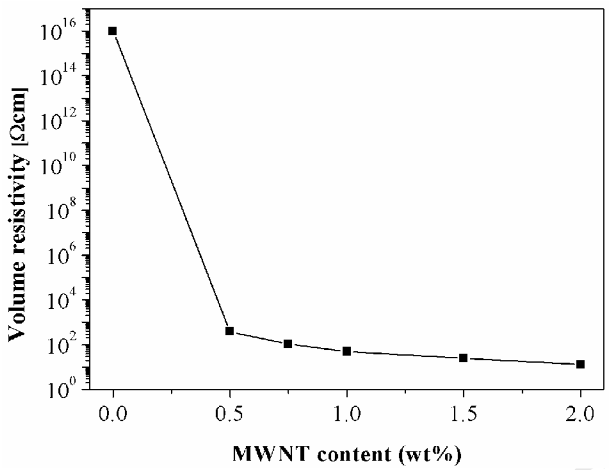


Fig. 2. Electrical resistivity of PLA/MWNT composites depending on the MWNT loading.

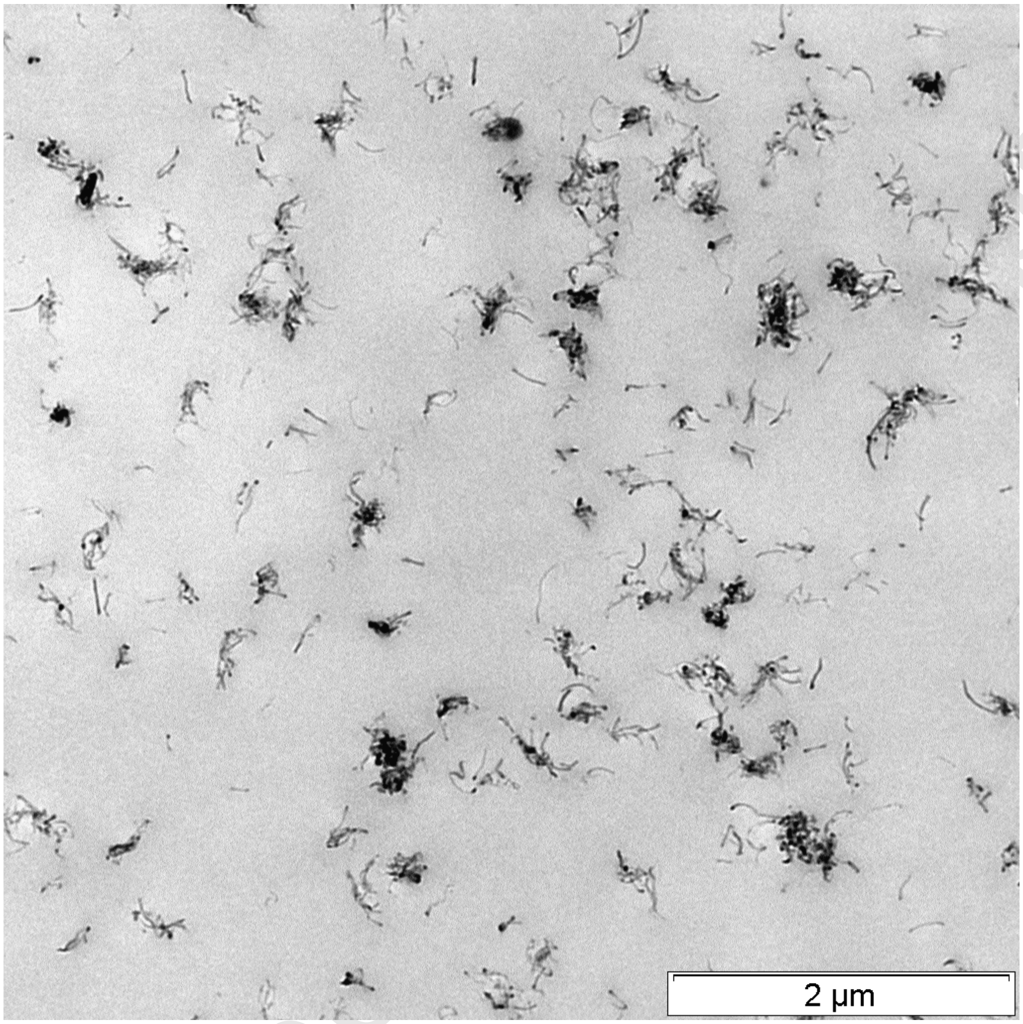


Fig. 3. TEM image of PLA/MWNT composite prepared at the MWNT loading of 0.75 wt%.

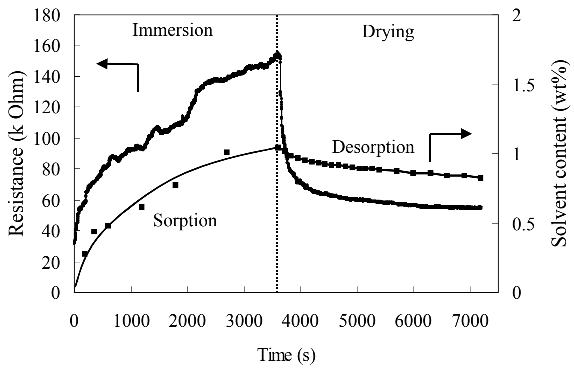


Fig. 4. Changes of the resistance and solvent content of PLA/MWNT composite (0.75 wt% loading, 0.5 mm thick) on contact of ethanol in 3600 sec solvent immersion/3600 sec drying process.

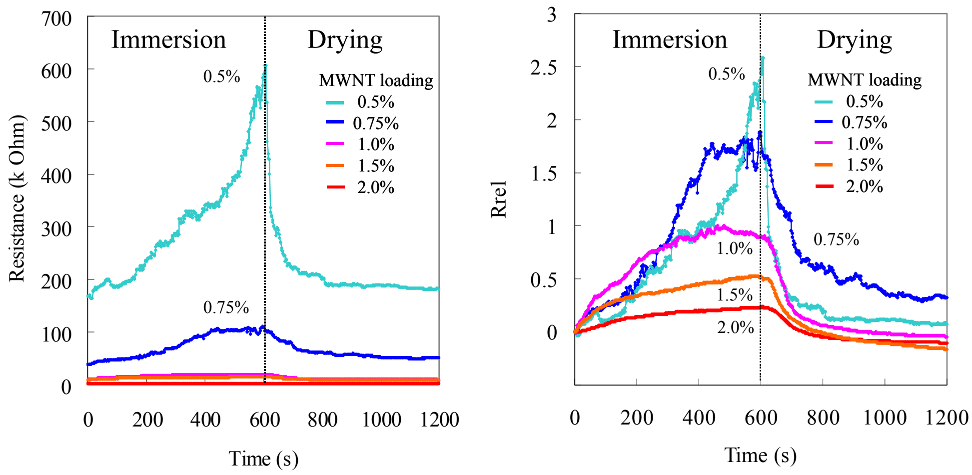


Fig. 5. Resistance changes of PLA/MWNT composites (0.5 mm thick) in ethanol, depending on MWNT loading.

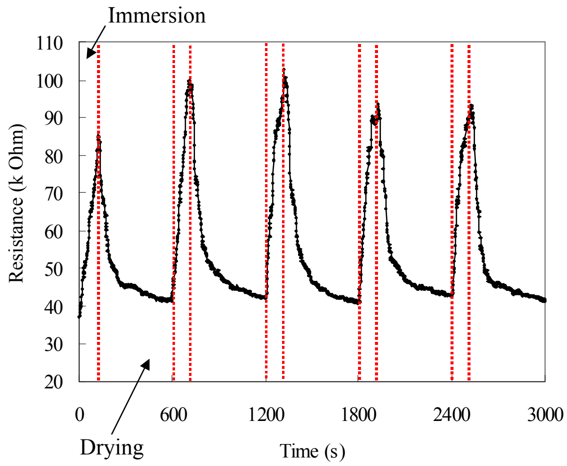


Fig. 6. Resistance change of PLA/MWNT composite (0.75 wt% loading, 0.5 mm thick) in ethanol.

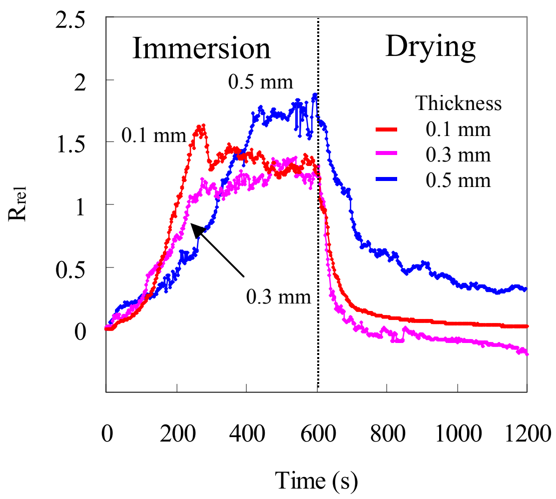


Fig. 7. Resistance changes of PLA/MWNT composites (0.75 wt% loading) in ethanol, depending on the sample thickness.

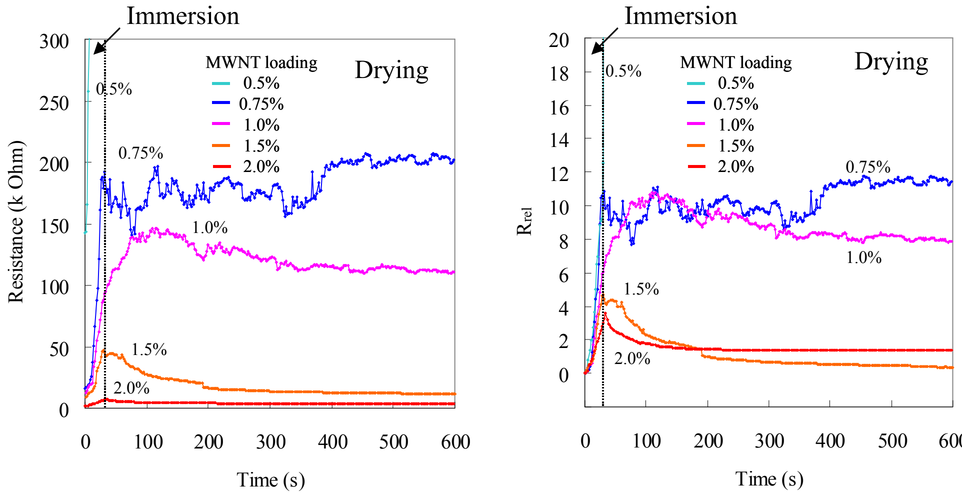


Fig. 8. Resistance changes of PLA/MWNT composites (0.5 mm thick) in chloroform, depending on MWNT loading.

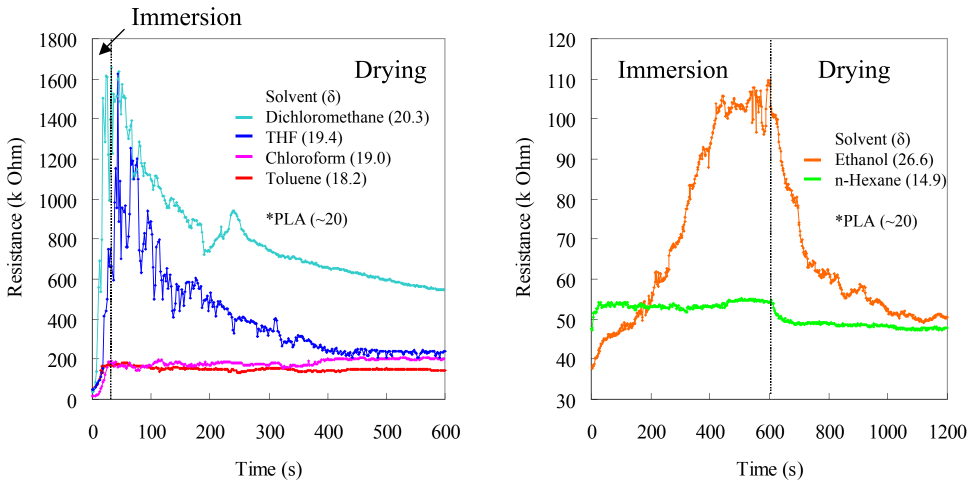


Fig. 9. Resistance changes of PLA/MWNT composite (0.75 wt% loading, 0.5 mm thick) in various solvents. The values of the solubility parameter δ in $MPa^{0.5}$ are given in parentheses.

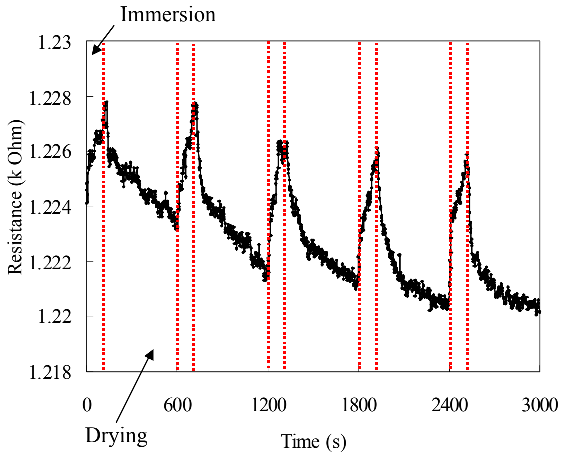
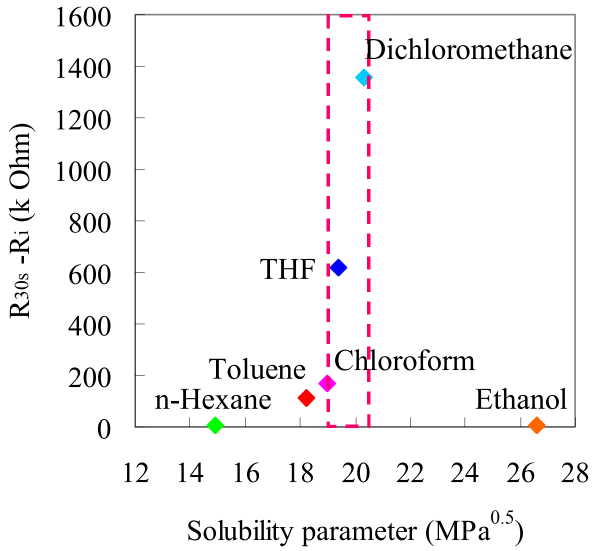


Fig. 10. Resistance change of PLA/MWNT composite (2.0 wt% loading, 0.5 mm thick) in water.



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