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Activation of the Electrical Conductivity on Non-Conductive MWCNT-Filled Plastic Moldings by Laser Processing

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Abstract

Two-phase polymer blends consisting of a polypropylene matrix and dispersed polycarbonate particles containing multi-walled carbon nanotubes (MWCNTs) have been injection molded. The obtained plastic moldings were patterned by laser treatment. The initially non-conductive molded plastic parts became electrically conductive in the treated areas after the laser treatment. Structures with line resistances of as low as 1.5 kΩ/ cm-1 were created on the surface of the parts. The dependency of the reachable resistance values on the parameters of the laser treatment, the material composition (the mass fraction of MWCNT in the polymer blend 3wt%...5wt%) as well as the injection molding parameters were investigated.

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Keywords: laser activation; electrical conductivity; polymer blends; carbon nanotubes; laser processing

1. Introduction

The necessity of combining the classical structural design of electronic circuits with 3D-components in recent years has led to the development of different technologies in the field of MID such as the 2-component injection moulding, hot embossing, film insert moulding, mask-lighting and Flamecon procedure as well as the laser-MID procedures [1-8]. MID stands for "Moulded Interconnect Devices" and describes electronic components where

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metallic conductive paths are applied onto prefabricated injection-moulded polymer carriers. The conductive paths are either created in a subtractive process through removing of a previously fully metallised surface or in an additive procedure through a selective surface treatment. The LDS-procedure is a very efficient method, where injection-moulded polymer carriers to which addition agents have been applied are structured by the laser [9]. These activated surface areas can be chemically copper-plated afterwards, followed by an electrolytically applied layer and finally a 3rd layer of precious metal. The classical MID-technology, however, has always required 4 - 5 partially complex process steps in order to create conductive paths.

The following article introduces an innovative method which enables the generation of conductive paths in only one activation process step. This method focuses on the space-resolved modification of the electric conductivity of normally insulating plastic parts by means of laser radiation. The principle is based on multi-phase polymer blends with matrix-disperse phase structures in which carbon nanotubes (CNTs) are located in the disperse phase (depots). The space-resolved activation brings the CNTs to the surface so that a conductive area - a conductive path - is generated. The first experimental results prove that this effect is mainly due to thermal and chemical transformation processes. Besides material composition and laser treatment parameters also the process parameters during the injection moulding influence process results in terms of the low resistance values to be reached.

2. Experimental

The investigations were carried out on polymer blends consisting of a polypropylene (PP)-matrix phase and a dispersed polycarbonate (PC)-phase, filled with carbon nanotubes (CNT). Industrial available Multiwall carbon nanotubes were used as CNT-material. The blend variants and their compositions are listed in table 1.

Table 1. Composition of polymer blends.

Sample	Content [wt%]		
	PP	PC	MWCNT
PC17	80	17	3
PC22	75	22	3
PC27	70	27	3
PC37	60	37	3
PC47	50	47	3

Injection-moulded plates with the dimensions (60 x 60 x 2.6) mm^3 were made from the polymer blends, on which then 2D-strukturing tests were carried out by means of laser radiation. 11 line structures with a length of 50mm and a distance of 5mm were generated on the plates (figure 1a). They were arranged either orthogonal or parallel to the injection moulding direction (flow direction).

a b

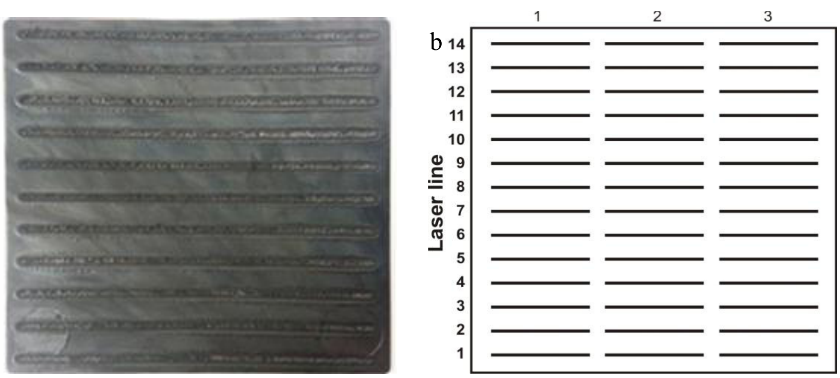


Fig. 1. Arrangement of laser lines; (a) Photograph of (60x60x2.6) mm^3 Standard – plate ; (b) Schematic representation of (150x150x2.6) mm^3 plates.

In order to gain results on the reproducibility over larger areas, 14 line structures in 3 columns were generated on

(150 x 150) mm^2 plates (figure 1b).

For the laser activation a 30W laser system (CO_2-laser; wave length 10.6µm) in combination with a 3D-scanning unit was used. Two parameter sets (PS) with different laser powers and scanning speeds were used for the laser structuring. PS 1 had an average power (45 %) and a scanning speed of $10mm \cdot s^{-1}$ and PS 2 a power reduced to 10 % and a minimised scanning speed of $2mm \cdot s^{-1}$. The laser beam was defocused and had a diameter of 1.6mm.

The morphology of the polymer blends was examined using a light microscope (Olympus BH-2; thin sections, thickness 5µm) as well as a scanning electron microscope (Zeiss Neon40 EsB) and a transmission electron microscope (Zeiss Libra200). The ultra-thin sections with a thickness of approximately 70nm were made at a temperature of -30°C using the Leica UC7 ultra-microtome. A Keithley electrometer 6517A in combination with the Keithley 8009 resistivity test fixture with annular electrodes was used to define the resistivity of the untreated injection-moulded test pieces. [10]

For the characterisation of the track geometry and the definition of depth and width of the laser activated lines the light microscope Keyence VHX-2000 was used.

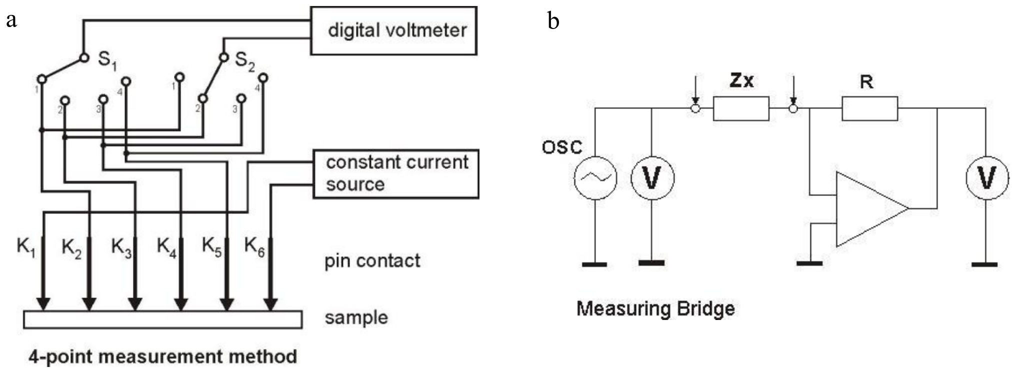


Fig. 2. Resistance Measurement Setup; (a) 4-point measuring method; (b) measuring bridge.

The electrical resistance in the lines was measured with the 4-point-method. So the track resistance could be determined in Ohm per length unit with an arrangement of six electrodes (figure 2a). Two of the electrodes (K_{1-6}) served as a constant current source. The voltage was measured via the remaining four electrodes (K_{2-4}) so that the resistance of the contacted line segments could be defined. The minimum measuring distance was 7.62mm.

Furthermore, a measuring device with an automatically balancing AC measuring bridge (Solatron 1260) was used to carry out measurements with a higher spatial resolution (figure 2b). A special motion system for the test samples enabled the gaining of measuring values in a raster of 1mm after repeated contact.

3. Results

The morphological examinations of the injection-moulded test pieces, illustrated by the example PC22, show a homogeneously distributed disperse phase (dark areas) in the matrix polymer (bright areas) for all blend variations (figure 3a). The TEM-image (figure 3b) shows that the disperse phase is the PC-phase in which the CNTs are selectively located. The higher the PC-content the larger the PC-CNT-phase is and it seems to become slightly stretched [10].

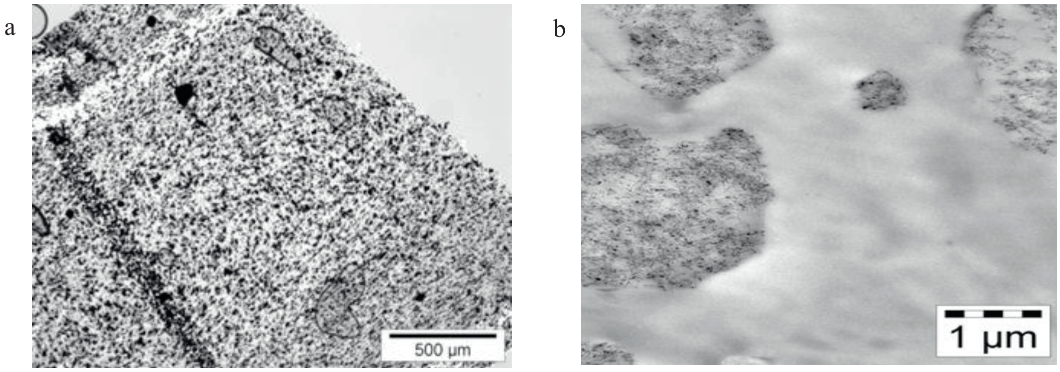


Fig. 3. Optical and transmission electron microscopy representing the blend morphology of sample PC22 [10]; (a) Optical micrographs of thin-section; (b) TEM-Image.

The partial laser treatment of the plates leads to a melting and/or sublimation of the polymer material resulting in linear structures (figure 1a). The lines have a V-shaped geometry with variably steep slopes and material bulging on the edge. The line depth and width vary depending on the laser parameters and the blend composition. Line depths of 80µm to 230µm (figure 4b) could be determined for parameter set 1. A reduced laser power and scanning speed (PS 2) leads to greater line depths ranging from 180µm to 370µm. In both cases the line depth diminishes with an increasing proportion of PC-CNT-phase.

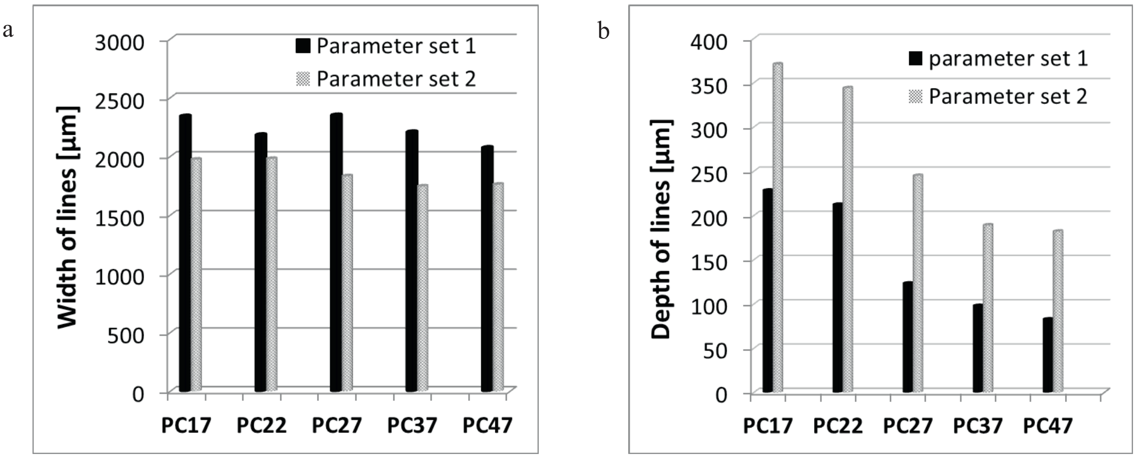
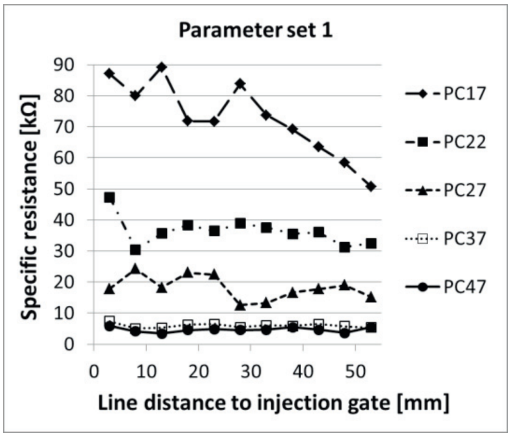


Fig. 4. Geometry of laser activated lines; (a) Width of lines; (b) Depth of lines.

The line width for PS 1 ranges from 2,070µm to 2,350µm and for PS 2 from 1,750µm to 2,000µm (figure 4a), which means that the lines with PS 2 are narrower than with PS 1. A dependence of line width and material composition cannot clearly be determined.

A laser treatment with the above-mentioned parameters leads in any case to an electrical conductivity of the activated areas. It depends on the laser parameters, the material composition, and the positioning of the lines on the plate. Figure 5a and 5b show the measured resistance values in the laser-activated lines which are arranged orthogonal to the flow direction. They range from ca. 2 to 40kΩ·cm^{-1} for both parameter sets. Resistance decreases the higher the PC-CNT-phase content is. In contrast to PS 1, the lines created with PS 2 show generally lower resistance values.

a



b

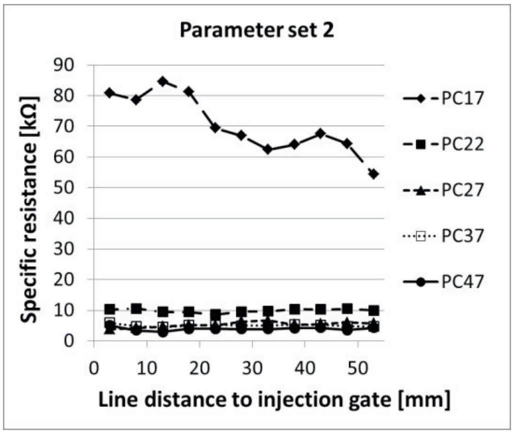


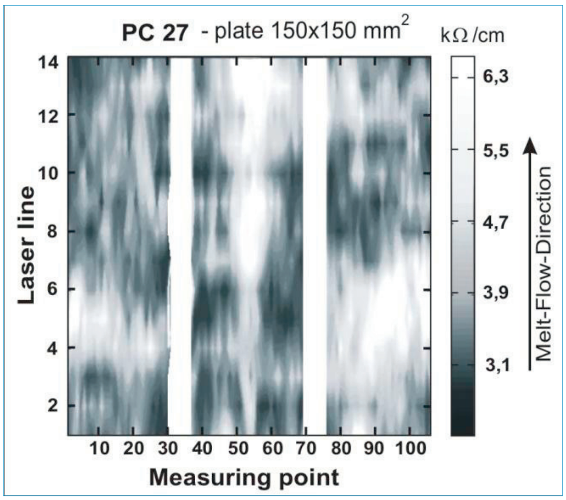
Fig. 5. Resistance of laser activated lines; (a) Parameter set 1; (b) Parameter set 2.

The resistance values of test samples PC22 and PC27 decreased significantly whereas those of test samples PC17, PC37 and PC47 differ only slightly after the change from PS1 to PS2. A dependence of the resistance on the line positions could be observed with test sample PC17 which implies that there are inhomogeneities of the PC-CNT-phase in the test sample.

In order to get detailed information on the scatter of the resistance values on the generated conductive paths over larger areas and to find a connection with the injection moulding, sample plates with the dimensions 150 x 150 mm^2 were injection-moulded and structured in the following step. Material sample PC27 was used for this and 14 lines in 3 columns generated on the plate surface (see fig.1b). Parameter set 2 was applied in this process.

The resistance values of the line arrangement were defined using the 4-point method as well as the higher resolving measuring arrangement with AC-bridge. An average resistance value of 967Ω/2.54mm was determined for all lines which equals a resistance value of 3.8kΩ/cm. Figure 6a illustrates the scatter of the resistance values. 10 tracks were measured in the individual laser lines which had a mean width of 1900µm. The deviation of the average resistance values was within a range of ±15 % (figure 6b).

a



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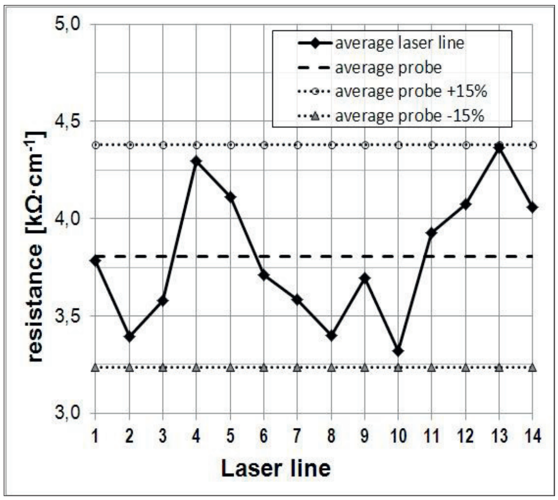
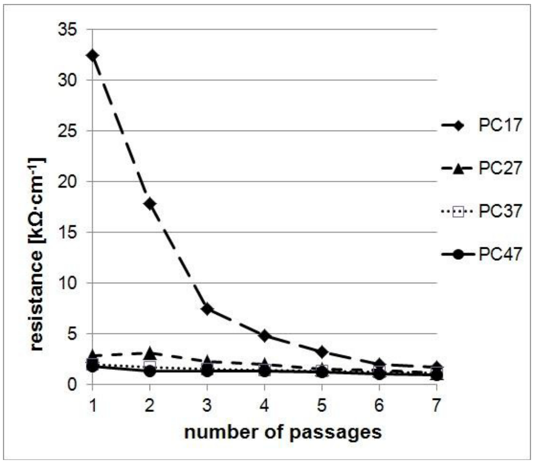


Fig. 6. Resistance values; (a) over the surface of the plate in the laser lines; (b) average values in the laser lines.

The results presented so far relate to the laser structuring with one passage over the material to generate a conductive path. Not only a material modification can increase the conductivity but also a repeated passage over the material geometry with the laser.

a



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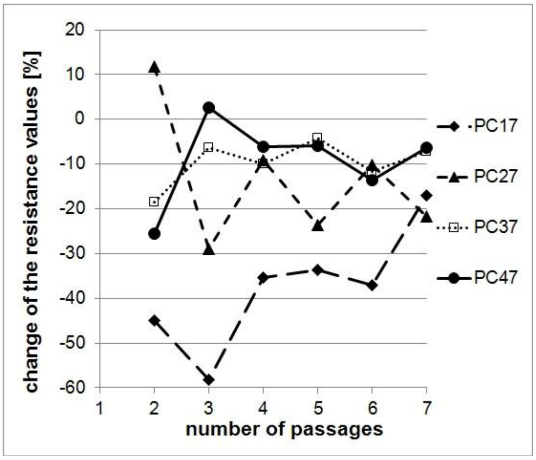

Fig. 7. Change of the values through multiple passages; (a) resistance absolut; (b) in percent.

This is illustrated on selected blends in fig. 7a. Basically, the resistance could be reduced continuously for all materials through multiple passages. The value of the resistance reduction depends on the polymer composition. Fig. 7b shows the change of the resistance values in per cent from one passage to the next. The lower the resistance after the first passage is, the smaller are the percental changes which can be achieved through subsequent passages.

The intense heat input into the plastic material resulting from multiple passages is disadvantageous and leads to a widening and deepening of the lines, and generally also to a distortion of the sample plate. Fig. 8 shows the changes to the line width and depth for material PC27.

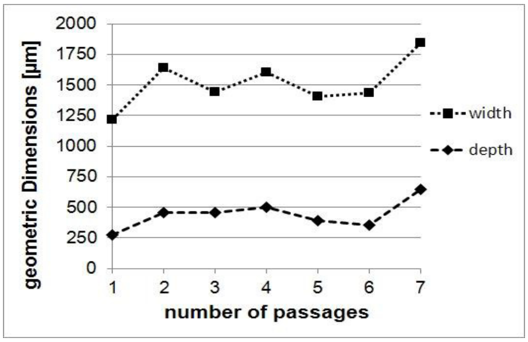

Fig. 8. Changes to the line width and depth through multiple passages.

4. Discussion

It can be assumed that the changes of the line depths and widths depending on the laser parameters are due to a different heat conductivity in the interaction zone of laser radiation and polymer blend. The energy input per unit length is similar for both parameter sets. Whereas with PS 1 the material is exposed to radiation just for a short time and the thermal energy reaches only near-surface areas, with PS 2 the material is exposed to laser radiation 10 times longer and the heat is conducted to deeper areas. This results in a greater line depth and thus a larger activated area of the V-shaped profile than with PS 1. Assuming that a conducting structure is created on the surface or in near-surface areas, a larger activated area induces a higher conductivity and thus lower resistance values. For blends with a PC-content of 37% and higher the resistance values for PS 1 and PS 2 become more and more similar. One can presume that electricity is not only conducted in near-surface areas but also deeper in the material.

Structuring the larger sample plates showed that the determined resistance values of the lines vary over the plate surface. Reasons can be either an inhomogeneous distribution of the PC-CNT-phases in the processed areas or a varying participation of lower material layers in the conduction of electricity. The reduction of the achieved resistance values with multiple passages speaks in favour of the second assumption.

The reduction of the line depth with an increasing content of PC-CNT-phase is a result of the higher melting and decomposition temperature which requires a higher energy input.

If the content of PC-CNT-phase increases, the distance between the phase particles decreases. This promotes the creation of a "conducting channel" through the impact of laser radiation, which finally leads to lower resistance values. The closer the phase particles are to each other the lower the influence of different laser parameters seems on the conductivity activation.

Conclusion

Electrically insulating polymer blends, consisting of a polypropylene matrix and a disperse polycarbonate phase filled with multi-walled carbon nanotubes (MWCNTs) were partially activated through IR-laser radiation. Electrically conducting line structures were created on the surface of injection-moulded test plates. Morphological examinations of the injection-moulded samples revealed a selective orientation of the CNTs in the PC-phase. An accumulation of MWCNTs could be detected in the laser lines, which enabled a space-resolved conductivity of the activated areas. Conductivity depends on the blend composition, the laser parameters and the arrangement of the lines on the sample body. An increasing PC-content of the polymer blends reduces the resistance of the laser-activated lines. A combination of low laser power and low scanning speed leads to a high conductivity.

The injection moulding process of the sample plates has a significant influence on the reproducibility of the achieved resistance values over the plate surface. Arranging the laser lines parallel or orthogonal to the flow direction of the polymer blend in the injection moulding process leads to different resistance values with all other conditions being the same. Further examinations regarding the injection moulding parameters are to clarify whether these differences result from variations in the density allocation of the PC-CNT-phase.

Acknowledgements

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