

THE APPLICATION OF THE SCANNING SPREADING RESISTANCE MICROSCOPY FOR THE MEASUREMENT OF THE SURFACE CONDUCTIVITY OF POLYPROPYLENE/GRAPHITE COMPOSITES

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Abstract

Electrically conductive composites with polymeric matrix (CPCs) and carbon based filler are the promising group of synthetic materials combining excellent mechanical properties of nonconductive matrix and electrical properties of conductive filler. These materials find application in many fields of interests such as an electromagnetic interference shielding, electro-optical devices, electrostatic discharge or signal transfer used in aerospace, marine, and automotive industries. Conductivity of CPCs can be positively or negatively influenced by many factors, such as change in external conditions, amount of conductive filler, etc. In this work, the changes of conductivity of CPCs with polypropylene matrix and conductive graphite filler are presented. Polypropylene/graphite (PP/graphite) composite was prepared via blending granulated PP, maleic anhydride grafted PP (MAH-g-PP) and natural graphite (either 65, 70 or 75 wt.%). It is obvious that the conductivity increases with increasing amount of conducting filler. The most conductive sample was thermally treated at 170°C for 1 hour or exposed to UV irradiation for 1 and 24 hours. The macroscopic conductivity disappeared and the changes in local current on the surface were studied using scanning spreading resistance microscopy (SSRM). SSRM shows that after the thermal treatment and UV irradiation the conductive areas disappeared and only residual current on the edge of the graphite particles was detected. Positive as well as the negative changes of conductivity of composites have a great influence on their further application.

Keywords: polymer composite, polypropylene, graphite, conductivity, scanning spreading resistance microscopy

1. INTRODUCTION

Conducting polymer composites are the promising group of synthetic materials which consist of nonconductive polymer matrix and conductive filler. These materials combine exceptional properties of both component and find application in many industrial fields such as an aerospace, automotive or medicine [1-3]. The carbon materials (i.e. graphite, carbon fibers or nanotubes, and carbon black) are widely used as the conductive fillers. Carbon fillers exhibit excellent electrical properties like a high conductivity and charge mobility. On the other side polypropylene (PP) is the thermoplastic polymer offering electrical and chemical resistance at higher temperatures and excellent mechanical properties. PP can be modified with graphite filler reinforcements to yield specific properties [4-8]. MAH grafted PP (MAH-g-PP) is suitable for improving interfacial adhesion between the carbon filler and PP [9].

Scanning spreading resistance microscopy (SSRM) is a useful technique based on atomic force microscopy (AFM). SSRM is used to study the changes in the surface conductivity of materials in the nanometer scale and localize the conductive and nonconductive components or areas of the sample surface [10-13]. It

operates in contact mode and the measurements take place at the constant bias voltage applied between the conductive tip and the conductive measured sample (**Fig. 1**). The current flowing between the tip and sample surface is measured simultaneously when the tip scans the surface. SSRM offers two dimensional imaging of local current distribution and appropriate images of contact topography. With respect to the nature of sample, the quality of the resulting images depends mainly on the value of the bias voltage applied between the tip and the sample, on the choice of the type of conducting layer on the tip, and on the probe with appropriate stiffness of the cantilever.

Conductivity is the fundamental property of this material and may be positively or negatively affected by many factors. The main aim of this work is to describe the influence of the filler amount and the changes of external conditions on the conductivity of PP/graphite composites and to show the SSRM as a suitable technique for the characterization of the surface conductivity.

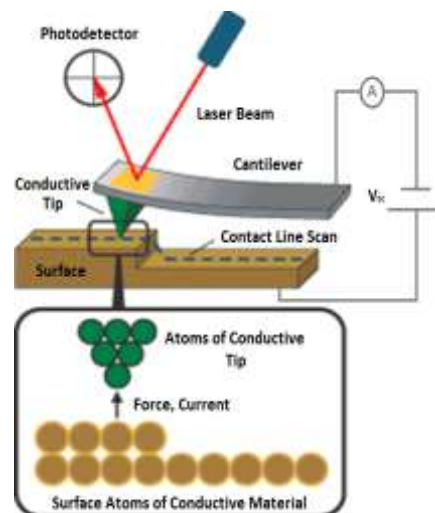


Fig. 1 The principle of SSRM measurement

2. EXPERIMENTAL

2.1. Materials and preparation of the samples

The commercial grade PP used as the polymer matrix was supplied from Yung Chia Chemical Ind., Co., Ltd., Taiwan. The natural graphite powder in the form of flakes was purchased from Graphite Týn s.r.o., Czech Republic.

The PP/graphite composites were prepared at the Tsinghua University, China. A certain amount of granulated PP and MAH-g-PP (15 wt.%) was mixed and transferred into the round bottom flask with the 300 ml of xylene. The mixture was dissolved by slowly heating to the temperature 130 °C. Then, a definite amount of the natural graphite (65, 70, 75 wt.%) was added. Three hours later, the mixture was transferred into acetone where composite started to precipitate. After the precipitation, composite was washed for three times with acetone and dried at 60 °C. The high speed disintegrator was used for the grinding the coarse-grained mixture into the powder. The obtained powder mixture was molded in 10x10x1.5 mm bar with a hot press at a temperature 180°C and pressure 8 MPa for 5 minutes.

2.2. Thermal and UV treatment

Samples were either thermally treated at temperature 170 °C for 1 hour (sample denoted as PP/graphite_170/1) in the laboratory drier Memmert UNE 300 or irradiated by UV light for 1 or 24 hours (samples denoted as PP/graphite_UV/1 or PP/graphite_UV/24) using the lamp Narva LT 36W/073 Blacklight blue containing UVB component. After heating the sample PP/graphite_170/1 was free-cooled to the room temperature.

2.3. Measuring methods

The special measuring apparatus (**Fig. 2**) was used for the measurement of macroscopic electrical conductivity. The measuring Cu-electrodes with triangular cross section were 47 mm apart and the conductivity of the samples has been measured by static applied voltage (1.000 ± 0.001 V) in DC regime. The conductivity was calculated from the mean value of electrical current passing through the sample. Obtained data were registered and processed in the original homemade software prepared in LabVIEW.

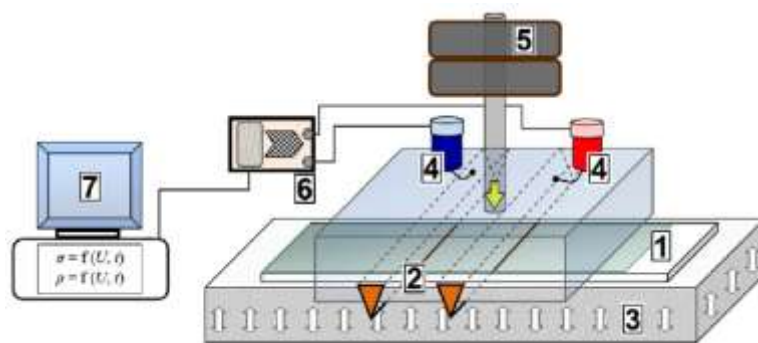


Fig. 2 Experimental apparatus for measuring the DC conductivity. (1) sample, (2) Cu-electrodes (distance 47 mm); (3) flexible insulator; (4) voltage terminals; (5) weights to ensure a constant load; (6) measuring card; (7) PC+ software

Local current maps of PP/graphite were obtained using SolverNEXT (NT-MDT) atomic force microscope (AFM) operated in the mode of SSRM. During SSRM constant bias voltage + 5 was applied between the measured conductive PP/graphite composite and conductive tip. SSRM was performed in contact mode with the contact probes with gold-coated tip CSG10/Au (NT-MDT).

The surface morphology was studied using the same SolverNext (NT-MDT) AFM operated in tapping mode with noncontact probes NSG30 (NT-MDT).

The images of morphology and local current maps were evaluated using Gwyddion software.

3. RESULTS AND DISCUSSION

3.1. Measurement of macroscopic and surface conductivity

Electrical conductivity of conducting polymer composites can be influenced by many factors such as shape and size of filler particles, amount and distribution of the filler in the matrix, changes of the external conditions. The macroscopic electrical conductivity of PP/graphite composites as a function of graphite content can be seen in **Fig. 3**. It is obvious that increasing amount of graphite filler caused increasing of conductivity. The maximum conductivity (149.5 S/m) were observed for the sample containing 75 wt.% of graphite. Therefore, only this most conductive sample was thermally and UV treated. After the thermal and UV treatment the negligible values of current ($< 1 \cdot 10^{-5}$ A) were measured.

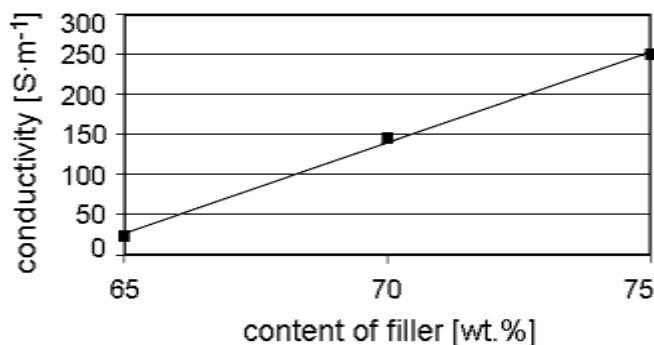


Fig. 3 Electrical conductivity values of PP/graphite nanocomposites for different content of graphite filler

The changes in the surface conductivity of PP/graphite composites at the nanometr scale were studied by SSRM. All results can be seen in **Fig. 4**. **Fig. 4a** shows the local current distribution of the original PP/graphite (75 wt.%), i.e. before the thermal and UV treatment. On this typical local current map the visible continuous conductive areas with the maximum of current about 50 – 80 nA can be observed.

After the modification (thermal treatment or UV irradiation) these areas disappeared and only the residual current is detected (**Fig. 4c, 4e, 4g**). The maximum of measured current ($\approx 16 - 19$ nA) are determined on the edge of the graphite particles, but these areas are extremely separated by regions of very low current. It

means that the thermal treatment and UV irradiation caused the changes of the surface resulting to decrease of the surface conductivity.

The morphology of the surface measured simultaneously in contact mode can be seen on **Fig. 4b, 4d, 4f, 4h**.

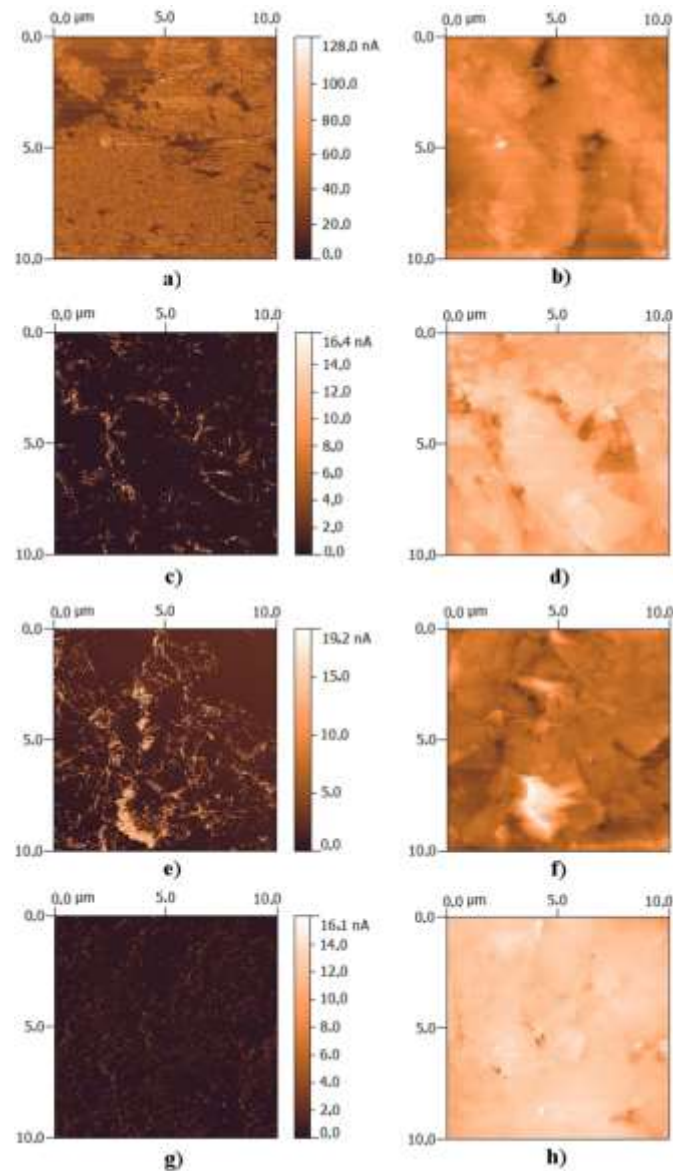


Fig. 4 AFM contact mode images of PP/graphite nanocomposite with 75 wt.% of the graphite. Original PP/graphite sample - a) local current map, b) morphology; PP/graphite_170/1 sample - c) local current map, d) morphology; PP/graphite_UV/1 sample - e) local current map, f) morphology; PP/graphite_UV/24 sample - g) local current map, h) morphology.

3.2. Measurement of morphology

Contact mode is characterized by a strong sample-tip interaction and in the case of PP/graphite composites it provided images with many visible artefacts (**Fig. 4b, 4d, 4f, 4h**). Therefore, more suitable AFM tapping mode was chosen for the imaging of the morphology. The results of tapping mode scanning are presented in **Fig. 5**. The flakes of natural graphite can be clearly seen for all samples and comparing with pristine PP/graphite composite no significant changes in the surface morphology were observed.

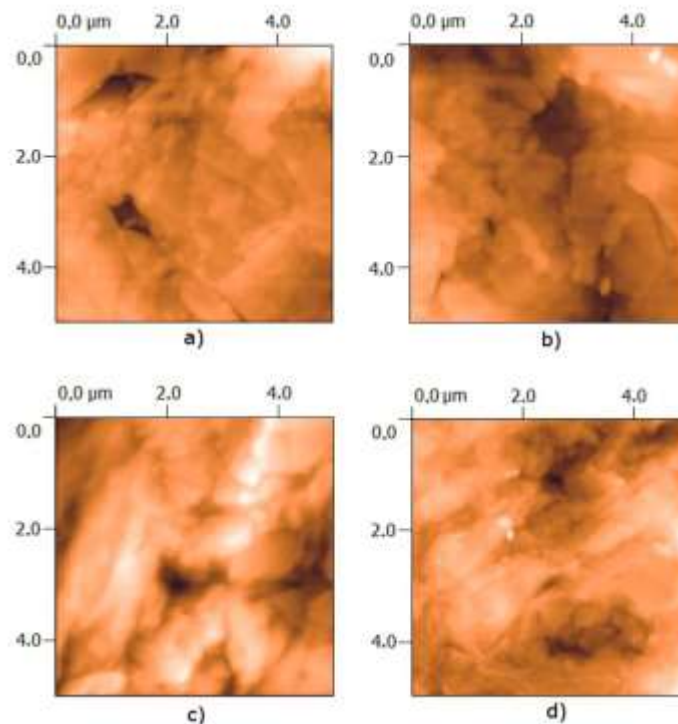


Fig. 5 AFM semicontact images show the surface morphology of PP/graphite nanocomposites with 75 wt.% of the graphite, a) original PP/graphite sample, b) PP/graphite_170/1 sample, c) PP/graphite_UV/1 sample, d) PP/graphite_UV/24 sample

4. CONCLUSION

Electrical conductivity of composites consisting of polypropylene (PP) matrix and graphite filler (PP/graphite composites) in dependence on the amount of the graphite filler and changes of external conditions was studied in this work. The PP/graphite composites were prepared and macroscopic conductivities of all these samples were measured and compared. The highest conductivity was observed for the sample containing 75 wt.% graphite which was subsequently thermally treated at the temperature 170 °C for 1 hour or UV irradiated for 1 and 24 hours. After these modifications the macroscopic conductivity disappeared. The decreasing of surface conductivity at the nanometer scale was detected using SSRM. Comparison of local current maps and images of morphology showed that the decrease in conductivity was caused by disappearing of conductive areas on the surface of modified samples. Present results clearly demonstrate that SSRM is a highly suitable technique for characterization of the conductivity and localization of the conductive and nonconductive areas of the solid samples.

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REFERENCES

- [1] J. LENG, X. LAN, Y. LIU, S. DU. Shape-Memory Polymers and Their Composites: Stimulus Methods and Applications. Progress in Materials Science, Vol. 56, 2011, pp. 1077-1135.

- [2] S. RAMAKRISHNA, J. MYER, E. WINTERMANTEL, K.W. LEONG. Biomedical Applications of Polymer-Composite Materials: A Review. *Composites Science and Technology*, Vol. 61, 2001, pp. 1189-1224.
- [3] Y.-Y. YU, W.-C. CHIEN, Y.-H. KO, C.-P. CHEN, C.-C. CHANG. Preparation of Conjugated Polymer-Based Composite Thin Film for Application in Solar Cell. *Thin Solid Films*, Vol. 584, 2015, pp. 363-368.
- [4] C. GARZÓN, H. PALZA. Electrical Behavior of Polypropylene Composites Melt Mixed With Carbon-Based Particles: Effect of the Kind of Particle and Annealing Process. *Composites Science Technology*, Vol. 99, 2014, pp. 117-123.
- [5] R. DWEIRI, J. SAHARI. Electrical Properties of Carbon-Based Polypropylene Composites For Bipolar Plates in Polymer Electrolyte Membrane Fuel Cell (PEMFC). *Journal of Power Sources*, Vol. 171, 2007, pp. 424-432.
- [6] V. CAUSIN, C. MAREGA, A. MARIGO, G. FERRARA, A. FERRARO. Morphological and Structural Characterization of Polypropylene/Conductive Graphite Nanocomposites. *European Polymer Journal*, Vol. 42, 2006, pp. 3153-3161.
- [7] A. KIRÁLY, F. RONKAY. Temperature Dependence of Electrical Properties in Conductive Polymer Composites. *Polymer Testing*, Vol. 43, 2015, pp. 154-162.
- [8] I. TCHMUTIN, A.T. PONOMARENKO, E.P. KRINICHNAYA, G.I. KOZUB, O.N. EFIMOV, Electrical Properties of Composites Based on Conjugated Polymers and Conductive Fillers. *Carbon*, Vol. 41, 2003, pp. 1391-1395.
- [9] J. U ROH, S. WON MA, W. II LEE, H. T. HAHN, D. WOO LEE, Electrical and Mechanical Properties of Graphite/Maleic Anhydride Grafted Polypropylene Nanocomposites. *Composites Part B-Engineering*, Vol. 45, 2013, pp. 1548-1553
- [10] G. BENSTETTER, R. BIBERGER, D. LIU. A Review of Advanced Scanning Probe Microscope Analysis of Functional Films and Semiconductor Devices. *Thin Solid Films*, Vol. 517, 2009, pp. 5100-5105.
- [11] P. DE WOLF, E. BRAZEL, A. ERICKSON. Electrical Characterization of Semiconductor Materials and Devices Using Scanning Probe Microscopy. *Materials Science In Semiconductor Processing*, Vol. 4, 2001, pp. 71-76.
- [12] S. DOERING, R. RUDOLF, M. PINKERT, H. ROETZ, C. WAGNER, S. ECKL, et al.. Scanning Spreading Resistance Microscopy for Failure Analysis of nLDMOS Devices with Decreased Breakdown Voltage. *Microelectronics Reliability*, Vol. 54, 2014, pp. 2128-2132.
- [13] C. JIANG, I.L. REPINS, C. BEALL, H.R. MOUTINHO, K. RAMANATHAN. Solar Energy Materials & Solar Cells Investigation of Micro-electrical Properties of Cu₂ZnSnSe₄ Thin Films Using Scanning Probe Microscopy. *Solar Energy Materials and Solar Cells*, Vol. 132, 2015, pp. 342-347.