Preparation of inverse nanoparticle-polymer composites by infiltrating monomers in indium tin oxide layers

<u>R. Hoffmann</u>^{1,2}, V. Baric^{3,4}, H. Naatz^{3,4}, L. Mädler^{3,4}, A. Hartwig^{1,2}

 ¹Fraunhofer Institute for Manufacturing Technology and Advanced Materials (IFAM), Wiener Str. 12, 28359 Bremen, Germany
²University of Bremen, Department 2 Biology / Chemistry, Leobener Str. 3, 28359 Bremen, Germany
³Leibniz Institute for Materials Engineering IWT, Badgasteiner Str. 3, 28359 Bremen, Germany
⁴University of Bremen, Faculty of Production Engineering, Badgasteiner Str. 1, 28359 Bremen, Germany
e-mail: ron.hoffmann@ifam.fraunhofer.de

Abstract: The limitations of low-fill nanoparticle-polymer composites are overcome through the initial creation of a stable, percolating inorganic nanoparticle scaffold with a very high porosity via flame-spray pyrolysis. Subsequently, the porous structures are filled with a monomer and are photochemically polymerized. It is shown that for indium tin oxide nanoparticles filled with a bifunctional acrylate, the electrical conductivity can be increased by one order of magnitude due to a structural changing of the layers.

Keywords: indium tin oxide (ITO), nanoparticle composite, inverse nanocomposite, flamespray pyrolysis, electrical conductivity.

Introduction

Through the linking of inorganic ceramic-like mixed-oxide nanoparticles with highly crosslinked thermoset systems, stiff, fracture resistant, and electrical as well as optoelectrical functional materials can be prepared [1]. Conventionally, surface modified nanoparticles are dispersed in either a polymer solution or a monomer, and from these dispersions films are created. Due to the particle properties, the nanoparticle composite films hereby achieved display a high degree of random aggregation of the particles in the composite [2]. In the work described here, nanoparticles comprising semi-conducting mixed transition metal oxides are embedded in a highly cross-linked thermoset matrix and are then maintained as low-fill yet highly percolating composite films [3]. Hereby, the nanoparticles are synthesized using flame-spray pyrolysis (FSP) [4] and are transferred in a further step to a secondary substrate via the layer-to-layer process [5]. Subsequently, there is an infiltration and a polymerization in the pores of the nanoparticle layer by a monomer. With nanoparticles from the flame-spray pyrolysis and capillary-driven monomer infiltration, inverse nanoparticle composite films should result, whereby the original particle scaffold structure and pore structure should be maintained while the electrical conductivity should be increased. Inverse nanocomposite is defined by us as a nanocomposite which is formed by first preparation of a particle scaffold which is afterwards infiltrated by the organic matrix material.

Experimental Procedure

For the preparation of inverse nanoparticle composite films, nanoparticles consisting of $In_{1.9}Sn_{0.1}O_3$ (ITO) were synthesized using flame-spray pyrolysis. The detailed preparation procedure for such nanoparticles can be found in the work of Kemmler et al. [6]. The nanoparticle layers were transferred to a substrate and prepared as electrodes using a conductive adhesive and contact electrodes under electrical resistance measurement with a digital multimeter so that the conductivity could be determined at ambient temperature. 1,6hexanediol diacrylate (HDDA) was used as monomer for infiltration of the porous scaffold, which is commercially available as Laromer[®] HDDA (BASF). To this the photoinitiator bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Omnirad 819 from IGM) was added. The infiltration and polymerization process can be found in Naatz et al. [7]. The samples thus achieved were examined via SEM, TGA, DMA, DSC, Raman, optical microscopy and resistance measurements.

Results and Discussion

The prepared nanoparticle composite film layers are transferred as thin films on glass slides with connected copper electrodes. During the individual preparation steps, the conductivity of the inverse nanocomposites was investigated using 2-point resistance measurement. As shown in Figure 1(a), the pure ITO nanoparticle layer has a conductance of 2.4 μ Scm⁻¹. After successful infiltration, the conductance increased by approximately one third to 3.3 μ Scm⁻¹. Due to capillary forces during the inflow of the liquid, it is expected that the particle scaffold is restructured. As the conductivity increases during infiltration with the monomer, one can conclude that the restructuration leads to an increase of particle-to-particle contacts serving as electric pathways.



Figure 1: (a) Conductivity of ITO nanoparticles after infiltration and curing with HDDA monomer; (b) microscopic image of homogeneously filled particle layer with monomer after UV curing

If the monomer is now photochemically polymerized inside the scaffold it shrinks and the cure shrinkage of acrylates might be up to 14 vol.% [8]. This cure shrinkage leads to a strong increase in number but especially intensity of particle-particle contacts. This leads to the observed strong increases of conductivity. The obtained value is $14 \,\mu\text{Scm}^{-1}$, which is an increase of one order of magnitude. The results show that the conductivity increases in each preparation step and it is surprising that addition of an insulating polymer increases the electrical conductivity significantly compared to the pure ITO layer. The results could be reproduced in four independent measurements. For clarity Figure 1 only shows the results for one of the series.

As presented in Figure 1(b), reflected microscopy examinations show that the polymer phase completely covers the ITO nanoparticles. Individual agglomerates of the nanoparticles as well as hair-like residues of the glass fiber filters used for the nanoparticle collection during flame-spray pyrolysis are visible in the image. The extensive coverage with resin, and thus the almost quantitative filling of the pores, was confirmed by TGA measurements.

Conclusions

Through a four-step process inverse nanocomposites could be prepared. First highly porous layers consisting of ITO nanoparticles were prepared by flame-spray pyrolysis. These layers were transferred onto glass surfaces, followed by imbibition with a monomer which was polymerized in the fourth step. Interestingly the electrical conductivity increases in each of these preparation steps although electrical insulating organic material is added. This is due to particle scaffold restructuration and cure shrinkage, both leading to an increase in the number of particle-particle contacts.

Acknowledgments

This study was funded by the German Research Foundation (DFG) under the funding numbers HA 2420/16-1 and MA 3333/10-1, for which we express our gratitude.

References

 H. Zhang, M. Popp, A. Hartwig, L. Mädler, Synthesis of polymer/inorganic nanocomposite films using highly porous inorganic scaffolds, Nanoscale 4 (2012) 2326–2332.
C.J. Capozzi, R.A. Gerhardt, Novel Percolation Mechanism in PMMA Matrix Composites Containing Segregated ITO Nanowire Networks, Adv. Funct. Mater. 17 (2007) 2515–2521.

[3] S.O. Schopf, A. Hartwig, U. Fritsching, L. Mädler, Imbibition into Highly Porous Layers of Aggregated Particles, Transp Porous Med 119 (2017) 119–141.

[4] W.Y. Teoh, R. Amal, L. Mädler, Flame spray pyrolysis: An enabling technology for nanoparticles design and fabrication, Nanoscale 2 (2010) 1324–1347.

[5] S.O. Schopf, S. Salameh, L. Mädler, Transfer of highly porous nanoparticle layers to various substrates through mechanical compression, Nanoscale 5 (2013) 3764–3772.

[6] J.A. Kemmler, S. Pokhrel, L. Mädler, U. Weimar, N. Bârsan, Flame spray pyrolysis for sensing at the nanoscale, Nanotechnology 24 (2013) 442001.

[7] H. Naatz, R. Hoffmann, A. Hartwig, F. La Mantia, S. Pokhrel, L. Mädler, Determination of the Flat Band Potential of Nanoparticles in Porous Electrodes by Blocking the Substrate–Electrolyte Contact, J. Phys. Chem. C 122 (2018) 2796–2805.

[8] J. Fouassier, J. Lalevée, Photochemical Production of Interpenetrating Polymer Networks; Simultaneous Initiation of Radical and Cationic Polymerization Reactions, Polymers 6 (2014) 2588–2610.