ABSTRACT

Doctoral dissertation of M.Sc. Eng. Krzysztof Szabliński entitled "Novel Polymer Composites Containing Modified Glass Microspheres for Selective Electroless Metallization"

The aim of the dissertation was to develop and characterize polymer composites based on acrylonitrile-butadiene-styrene (ABS) and polylactide (PLA), filled with glass microspheres modified with biomimetic layers derived from polydopamine (PDA) or tannic acid (PTA), and subsequently activated with silver. These materials were designed for selective electroless metallization after prior laser activation of the surface. It was assumed that such systems would enable the fabrication of low-density materials that retain their insulating character in the bulk while exhibiting local surface conductivity in areas activated by laser radiation and coated with a Cu layer.

Glass microspheres with two particle-size ranges were used in the study: M (30-105 μm) and M2 (1000-2000 μm). PDA or PTA layers were deposited on their surface, followed by Ag, resulting in MDAg, MTAg, M2DAg and M2TAg microspheres. ABS- and PLA-based composites containing 10-30 vol.% filler were prepared by compression molding. The surfaces of the samples were activated using an Nd laser (1064 nm) and then subjected to electroless metallization in a Circuposit™ 3350 Cu bath. The characterization of the materials was based on density measurements, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), melt mass-flow rate (MFR) measurements, wettability and surface free energy (SFE) tests, static tensile tests, impact strength tests, dynamic mechanical analysis (DMA), observations using optical microscopy and scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM/EDS), as well as measurements of surface resistivity (ρ_s) and through-plane resistivity (ρ_v).

It was shown that the M microspheres with a smaller diameter were the more favorable filler, as they provided a more homogeneous distribution in the matrix and enabled the formation of continuous Cu tracks after laser activation. The M2 microspheres did not allow a homogeneous composite structure or continuous Cu layers to be obtained. FTIR and SEM/EDS analyses confirmed the successful deposition of PDA/PTA layers and Ag on the surface of the microspheres. TGA and DSC studies showed that the incorporation of MDAg and MTAg microspheres affected the thermal stability and thermal transitions of the composites, with this effect being more pronounced in PLA-based materials than in ABS-based systems. In the case of PLA, the filler content also affected the cold crystallization enthalpy ΔH_{cc}, melting enthalpy

ΔH_m and degree of crystallinity X_c, indicating the possibility of tailoring the structure and properties of the material as a function of the microsphere content. Density measurements confirmed the possibility of obtaining materials with relatively low density, while MFR results showed that, despite a decrease in melt flowability, particularly in PLA-based composites, the materials remained suitable for further processing. Wettability and SFE tests showed that the presence of Ag-activated microspheres changed the surface character of the composites, which was important for the subsequent metallization process.

The selected composites, i.e. ABS_MDAg30, ABS_MTAg30, PLA_MDAg10, PLA_MDAg20, PLA_MDAg30 and PLA_MTAg30, showed susceptibility to selective metallization. Macroscopic and microscopic observations, together with SEM/EDS analysis, confirmed that laser activation led to local modification of the surface layer, exposure of microspheres located close to the surface, and the creation of conditions suitable for the subsequent formation of a Cu layer in the activated areas. In the track regions, ρ_s was reduced by several orders of magnitude, while high ρ_v values were maintained in the direction perpendicular to the surface. It was also demonstrated that systems containing MDAg microspheres were generally more effective in initiating metallization than systems containing MTAg microspheres. Static tensile tests, impact strength tests and DMA showed that the incorporation of microspheres affected the functional properties of the composites, with increasing filler content generally leading to reduced strength, limited deformability and lower impact strength.

The conducted studies confirmed the thesis of the dissertation. The developed ABS- and PLA-based composites containing MDAg and MTAg microspheres constitute lightweight polymer materials that enable the selective formation of Cu tracks after laser activation and electroless metallization, while maintaining the insulating character of the material bulk. These systems may provide a basis for further work on filaments for FDM 3D printing, injection-molded components and 3D-MID structures requiring the integration of load-bearing, insulating and conductive functions within a single material.