POLITECHNIKA ŚLĄSKA W GLIWICACH

Wydział Mechaniczny Technologiczny

Bartłomiej Jagodziński

NOWE PREKURSORY METALIZOWANIA BEZPRĄDOWEGO MATERIAŁÓW POLIMEROWYCH MODYFIKOWANYCH LASEROWO

ROZPRAWA DOKTORSKA

Promotor
Dr hab. n. t. Piotr Rytlewski, prof. UKW
Promotor pomocniczy
Dr hab. inż. Krzysztof Moraczewski, prof. UKW

Gliwice 2018

SUMMARY

The subject of this doctoral dissertation was to extend knowledge about the possibilities of using new precursors for metallization of laser-activated polymer coatings. The precursors used were new copper complexes in the form of:

a) poly- di(L-tyrosine) copper (II) – further referred to as compound A,
b) 7.5 hydrate chromate (IV) tris (2,2'- dipyridyl) copper (II), further referred to as compound B
c) methanol di (2,2'-dipirydylu) sulfate (VI) copper (II) - further referred to as compound C.

The first part of the dissertation presents a critical analysis of the current state of knowledge, which describes, among others, some methods of metallization of polymeric materials, physical methods (plasma and laser modifications) for modifying the surface layer of polymeric materials as well as precursors commonly used in electroless metallization of polymeric materials. Based on the analysis, the dissertation, purpose and scope of the dissertation were formulated, including the methodology of the research.

Experimental research has been divided into two parts. The first one was preliminary research, the aim of which was to select the base materials and polymer coatings and to determine the mechanisms of thermal degradation of the studied copper complexes. The second part was the main research, the aim of which was to assess the possibility of using the copper complexes studied as precursors for metallization of electroless laser-irradiated coatings. The main research included, in particular, the determination of: the type and percentage of copper complexes comprised in polymer coatings, the effects of laser radiation parameters on the of physical and chemical structure changes of coatings and of copper layers deposited by means of electroless matallization.

In experimental studies, epoxy, polyurethane and acrylic-polyvinyl resins were used as the matrix for the technical coatings intended for metallization. In addition to the copper complexes, the coatings also contained glass microspheres of various sizes. The coatings were applied on the substrate of selected polymer materials (polycarbonate, polystyrene, polypropylene and polylactide) produced by injection molding.

The coatings were irradiated using an ArF excimer laser and different doses of irradiation (unit energy and number of laser pulses). After irradiation, the samples were metallized using a six-component both Copper-85electroless metallization copper-plating (MacDermid, USA) with formaldehyde as a reducing agent.

Numerous experimental techniques, including thermogravimetry with FTIR spectroscopic analysis (TGA-FTIR) of thermal degradation products, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), X-ray energy dispersive microanalysis (EDX), photoelectron spectroscopy (XPS), UV-Vis spectroscopy, contact angle measurements and free surface energy calculations, adhesive strength tests have been performed.

It was found, based on experimental investigations, that from the group of three copper complexes studied, complex A (copper L-tyrosine) proved to be the most effective for electroless metallization, while on the other hand, complexes B and C containing low molecular weight compounds whose thermal separation energy from the complex structure is smaller than organic copper ligands are not effective precursors for electroless metallization.

Modification of the surface layer of coatings with the ArF laser resulted in a conicalilike geometrical surface structure. At the tops of the cones there copper was detected, which was formed as a result laser-induced degradation of complex A. The increase in unit energy and the number of pulses increased the height of the cones and the content of precipitated copper in the surface layer of coatings. Copper agglomerates formed by irradiation with laser pulses were largely oxidized, which was confirmed by XPS analysis. With irradiation doses, the amount of copper in the form of Cu (0) and CuO increased, while the amount of copper in the form of Cu_2O decreased. In all cases of adhesion testing the interface between polymer substrate/coating or copper glue was broken. The use of glass microspheres enabled to reduction of the content of A complex sufficient for electroless metallization of coatings.. It was shown that copper agglomerated on the surface of glass microspheres as a result of laser irradiation.

The obtained test results are original and are the subject of two patent applications in the Polish Patent Office.