ASSESSMENT OF POLYMER DEGRADATION BY THE COMBINED USE OF LIBS AND LA-ICP-MS

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1. INTRODUCTION

Synthetic polymers are nowadays widely used in a variety of applications, ranging from food packaging, construction materials to the housing of electronic devices. In general, the applied synthetic polymers are composed of an organic-carbon-chain polymer and different additives that give the materials the intended chemical and physical properties. Commonly applied additives include plasticizers, antioxidants, antistatic agents, lubricants, flame retardants or inorganic pigments.

During application, polymers are often exposed to harmful environmental conditions, causing changes in their chemical composition. In this context, the negative influences of sunlight but also contact with ambient gases and environmental liquids have to be mentioned. Whereas UV light and oxidative gases are known to promote degradation, corrosive gases or metals dissolved in rain, snow and river or sea-water are susceptible for uptake into the polymer network, resulting in increased concentrations of inorganic constituents in aged materials. All of these possible interactions contribute to unwanted changes in the polymer composition, which finally lead to altered material properties (e.g. bleaching of colors, reduced thermal stability, increased brittleness, etc.). Thus, analysis of synthetic polymers is experiencing growing interest due to increased environmental regulations and the need for sustainable polymer recycling strategies.

Traditional methods for the investigation of polymer degradation are FT-IR and Raman spectroscopy. Furthermore, Pyrolytic-GC-MS, MALDI-ToF–MS, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are frequently used techniques. Although well established, these techniques cannot provide the entire information required for thorough material analysis. In particular, with the aforementioned techniques sample analysis is limited to bulk investigations or surface near regions only. Additionally, detection of metal content within polymers with a high sensitivity is not feasible. These shortcomings could be circumvented with the use of LIBS and LA-ICP-MS. In the field of polymer analysis, broadband LIBS spectra have already been used for the identification [Sattmann 1998] and classification [Haddad 2014] of different polymer types. Additional benefits of LIBS are the possibility to perform spatially resolved analysis such as depth profile measurements.

In this contribution, we report the use of LIBS for assessment of polymer degradation. Moreover, the uptake of contaminations from the surrounding environment has been determined using LA-ICP-MS. The developed Tandem LA-ICP-MS/LIBS approach for polymer analysis has been applied for two different research tasks:

- Objects of art and cultural heritage are sometimes exposed to harsh environmental conditions. The permanent exposure to humidity, UV-radiation and corrosive gases results in the degradation of valuable artwork. As the fundamentals of the degradation process are still not completely understood, knowledge about durability and aging properties of applied art materials is of particular interest.

- At the end of their life-cycle, polymers often end up in the environment, for example in the form of microplastics which pose a significant threat to various ecosystems. Accordingly, the composition and metal contents of the degraded polymers should be monitored, to better estimate the adverse health effects of microplastics in the environment.

2. EXPERIMENTAL

A LIBS system (Model J200) equipped with a 266 nm Nd: YAG laser by Applied Spectra, Inc. (West Sacramento, California) was used for LIBS analysis. For collection and spectroscopic analysis of the radiation emitted by the laser-induced plasma, an optical fiber system connected to a Czerny-Turner spectrometer with six-channel CCD detection was employed. ICP-MS analysis of the generated aerosol was performed using a Thermo iCAP Qc quadrupole ICP-MS device (ThermoFisher Scientific, Bremen, Germany). Connection of the tandem LA/LIBS system to the mass spectrometer was achieved using PTFE tubing.

Modern paints composed of inorganic pigments and organic binders were prepared by mixing Alkyd Medium 4 (Lukas®, Germany) with 9 inorganic pigments (Kremer Pigmente, Germany). The pigment/binder ratio chosen was 1:3, prepared paint mixtures were cast on glass slides with a wet film thickness of approx. 150 μm. Sample drying was conducted at ambient conditions for 1 week. Accelerated stress tests were performed to cause degradation of the polymers as well as uptake of sulfur within the investigated samples. Therefore, samples were exposed to synthetic air in combination with corrosive gases (SO_2, H_2S and O_3) or UV light in a weathering chamber [Wiesinger 2010].

Degradation of commercial polystyrene thin films obtained from Goodfellow Inc. (Hamburg, Germany) was conducted by sample exposure to UV radiation and the concurrent treatment with oxidizing agents (H_2O_2 and HNO_3). Careful optimization of the process parameters ensured successful and reproducible degradation of the

investigated micro-plastics. The degree of sample degradation was determined using FTIR spectroscopy and LIBS analysis. Subsequently sorption experiments with the aged polystyrene thin films were performed, with the aim to investigate the temporal behavior of trace metal uptake. Aged polymer samples as well as unaged blank samples were exposed for different times to artificial seawater containing defined concentrations of selected trace metals.

3. RESULTS AND DISCUSSION

3.1. Degradation of modern art materials

Aim of this study was to test the feasibility of LIBS for measurement of polymer degradation and to confirm the uptake of sulfur with LA-ICP-MS of modern art materials consisting of a polymeric binder and inorganic pigments. Unlike most currently employed techniques for polymer characterization, these two are not limited to the surface but also enable depth profiling.

Using LIBS in combination with advanced data evaluation procedures, changes in the polymer composition due to weathering with corrosive gases and UV light was observed. Performing depth profiles on various samples exposed to different corrosive conditions, the influence and severity of these conditions on the degradation of the modern art material was assessed.

LA-ICP-MS parameters were optimized for the qualitative measurement of gas permeability into the investigated modern art material. The acquisition of depth profiles was successful. Again, the influence of different corrosive conditions on the sulfur uptake was investigated. These experiments revealed a high variation of the degree of sulfur uptake depending on the aging conditions. Additionally, sulfur uptake was not only observed in surface near regions of the investigated modern art material but also diffusion profiles into the bulk material were observed.

3.2. Artificial micro-plastic samples

FTIR measurements of the aged polystyrene samples revealed significant changes in the main polymer absorbance bands, in particular when compared to unaged reference samples. This outcome could be confirmed with LIBS, showing a significant increase in the intensity of the oxygen emission line at 777 nm, indicating partial oxidation of the polymer samples.

Samples derived from the sorption experiments were analyzed using tandem LA/LIBS-system, particular attention has been paid to determine the distribution of the absorbed metals within the polymer films. Depth profiles reveal that uptake of trace metals did not only occur on the sample surface, even in the underlying bulk material significant differences to the reference samples were observed. Thus, measurement of the sample surface is insufficient for assessment of total metal contents in aged polymer

films, instead analysis over the whole film thickness is required. Moreover, the measured uptake of the toxic trace metal Cd could be directly correlated with the information obtained for degradation and oxidation of the polymer sample.

4. CONCLUSIONS

A Tandem LA/LIBS approach has been successfully employed for assessment of polymer degradation and measurement of gas or metal uptake from ambient environment. In recent studies the occurrence of molecular emission lines in broadband LIBS spectra has been successfully used for identification and classification of polymers, here we demonstrated that measurement of these lines enables also the detection of polymer degradation. Analysis of the generated aerosol with ICP-MS has been shown to provide the sensitivity required for the determination of sample constituents present in traces only, such as corrosive gases used in the weathering experiments with modern art materials or the trace metals used in the sorption experiments performed with aged micro-plastics.

Analysis of aged modern art materials suggest that UV exposure or pretreatment with O_3 significantly influences the polymer permeability for SO_2 and leads to observable degradation of the polymeric binder material. As the capabilities and limitations of LIBS and LA-ICP-MS have been assessed, a multitude of additional experiments would be of interest to retrieve more comprehensive insights into the aging process of the investigated material.

Application of the proposed tandem LA/LIBS procedure for the analysis of aged micro-plastics has been found to be beneficial. This approach provides information about the extent of polymer degradation but also data about the distribution of the metals within the investigated polymer thin films. Thus, current knowledge about the interaction of trace metals with micro-plastics could be improved. In particular it could be shown that increased degradation of micro-plastics results in elevated trace metal uptake. Moreover, metal uptake is not limited to the sample surface only, even for the bulk material enhanced concentration levels were found.

5. ACKNOWLEDGEMENTS

6. REFERENCES

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