Abstract

Poly(vinyl chloride) (PVC) objects make up a significant part of contemporary heritage collections. PVC was identified as one of the polymeric materials that are prone to degradation, making it necessary to conduct further studies for an improved understanding of the mechanisms of degradation. PVC objects can become part of collections long after their lifetime, as defined by industrial standards, has ended. The aim of this work was to first develop analytical methods for a more comprehensive characterisation of PVC objects. So far, the chemical composition (identity and content of plasticizers, polymer molar mass and branching) remains largely unknown for objects in heritage collections. To overcome this gap, analytical methods were developed, validated, and then applied to many diverse PVC objects found in a reference collection at the Faculty of Chemistry and Chemical Technology, University of Ljubljana. Gas chromatography with a mass spectrometric detector or a flame ionisation detector (GC-MS and GC-FID) was used for a qualitative and quantitative determination of plasticizers in more than 100 objects. Near-infrared and ATR mid-infrared spectra of the objects were collected non-destructively to create classification and regression models for a quick characterisation of plasticizers in collection objects. Machine learning-supported classification algorithms (Linear Discriminant Analysis (LDA), Naïve Bayes Classification (NBC), Support Vector Machines (SVM), k-nearest neighbours (kNN), decision trees (DT), and Extreme gradient boosted decision trees (XGBDT)), were successfully used to identify the plasticizers in the object. Partial least squares regression was used to determine the content of di(2-ethylhexyl) phthalate and dioctyl terephthalate in PVC objects. Accurate determination of PVC's molar mass by size-exclusion chromatography with multi-angle light scattering detection required optimising the sample preparation procedure. The optimised method was used to describe the ranges and the distribution of molar mass of historical and contemporary PVC objects and used to investigate changes in molar mass due to accelerated degradation. The main goal of my research was to model the degradation of PVC by developing a damage function, which evaluates the contribution of variables to the yellowing of transparent PVC objects. Elimination of hydrogen chloride from PVC leads to the formation of polyene sequences, resulting in yellowing of the material. Objects from a reference collection were exposed to accelerated degradation experiments, characterised with the developed analytical methods, and the yellowing was expressed as a rate of increasing the value of the b* coordinate in the CIEL*a*b* colour space. Higher temperature and relative humidity increased the degradation rate, while higher plasticizer content and polymer molar mass decreased it. The activation energy of the yellowing was calculated as (86 ± 3) kJ/mol. The lifetime of a PVC object, based on perceptible colour change, can be predicted from its properties and the environmental conditions of storage. Understanding the contribution of variables to degradation can help prioritise conservation efforts and resource allocation in heritage collections of modern materials.