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Thermal Stability of Organic Coatings for Aluminium and Its Environmental Aspects

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Thermal stability of organic coatings for aluminum plays a key role not only in specific applica-tions, but also in the recycling process of aluminum scrap. For production of secondary alumi-num it is necessary to remove coatings from scrap. Rests of unremoved coatings affect the qual-ity of final aluminum. Most of methods for coatings removing are based on thermal decomposi-tion. This process leads to emission of various organic compounds which present potential risk for human health and also for environment. Thermal stability of all tested coatings with in-creasing temperature was study with use of thermogravimetric analysis (TGA). Significant deg-radation of coating started at temperature 200 °C and at temperature 450 °C was most of the tested coating degraded and remained only inorganic part of coating. Inorganic part render ap-prox. 30 % of the original coating mass. Degradation of tested coatings was also confirmed by Fourier transform infrared spectroscopy (FTIR) analysis. This work also deals with study of in-organic/organic ratio of hybrid coating on real sample of scrap for recycling. The thermolabile part of coating is degraded during heating, which lead to emission of organic compounds and products of degradation which can affect human health and also the environment.

Keywords: Organic Coating, TGA, FTIR, Thermal Stability

1 Introduction

The surface of aluminum products is usually covered with organic based coatings. The purpose of these coatings is based on hydrophobicity, corrosion resistance and also have a positive visual effect, because an unsightly layer of aluminum oxide is not form on it. The composition of organic coatings varies according to the end use and the required properties of the aluminum products. Nowadays, hybrid coatings are the most widely used, these coatings consist of an inorganic and an organic component. These coatings have low permeation properties and their structure is highly crosslinked (Zheng et al., 2010). Most commonly, various types of organosilanes are, used as organic component, e.g. 3 glycidoxypropyl-trimethoxysilane, tetramethoxy silane (Zandi-zand et al., 2005), amino-terminated polydimethylsiloxane (Wu et al., 2007). Modified silanes, known as Ormosil are very often used. Ormosil is the designation for alkyl substituted silanes in which a linear or branched hydrocarbon radical (n-propyl, n- butyl, i-butyl, i-octyl) is, used as the alkyl group (Metroke et al., 2004). It is also possible to use a polymer consisting of dopamine (Ou et al., 2004). To improve the anticorrosion properties or to achieve the re-quired properties, such as hydrophobicity, it is possible to add some other compounds to the mixture of precursors forming own coating. It can be, for example, a perfluoro poly-mer, which significantly affects the hydrophobicity of the coating (Wankhede et al., 2013), it is also possible to add zeolite, which increases the corrosion resistance (Calabrese et al., 2014). To increase the anticorrosion properties, it is possible to add some inorganic com-ponents, such as titanium dioxide, cerium dioxide, zirconium tetrapropoxid (Wu et al., 2007; Voevodin et al., 2001). Polytetrafluorethylene can also be used as a coating for alu-minum, this coating has among others also icephobic properties (Menini et al., 2011). It is clear that hybrid (organic-inorganic) coatings may contain other organic compounds, which improved its properties. The organic compounds presented in these coatings are not thermostable and degradation of coating can be observed at elevated temperature. This degradation is usually accompanied by evolving of toxic gases. These gases consist of volatile compounds present in the coatings and/or their degradation or oxidation product. Organic coatings can cause several problems with aluminum recycling. The preparation of secondary aluminum is based on heating the aluminum packet (which should be recy-cled) up to 700 °C. The thermal stability of coatings is very important when coatings are applied to products that are intended to ambience with high temperature. Thermal load-ing and degradation of coatings affect mechanical properties such as roughness (Lysoňková et al. 2018). Information on thermal stability is also very important in the pro-cess of recycling and production of the secondary aluminum. Thermolabile coatings can release toxic gases that significantly affect human health and, on the other hand, the rest of the coatings can affect the quality of secondary aluminum. Many toxic compounds, such as dibenzofurans, polychlorinated dibenzo-p-dioxins can be released during heating of hybrid (Lee et al., 2005; Ba et al., 2009; Chen et al., 2004). For this reason, most coatings must be removed before recycling. In this work, TGA (thermogravimetric analysis) and FTIR analysis (infrared spectroscopy with Fourier transformation) were used to study the thermal stability of coatings.

2 Materials and methods

Sample of coatings were taken from real packets of aluminum waste, which was destined to recycling. Two samples with different coatings were selected, the first was white and the second was grey. The samples represented most commonly used polysiloxane coat-ings. Each coating was washed with acetone to de-grease before being removed from the aluminum ma-trix. Separated coatings without aluminum matrix were used for analysis. The removal of coatings was ensured by mechanical way. The original samples sep-arated from the original aluminum packet with coat-ings are shown in the figure 1. The white coating is based on a synthetic paint based on fenylme-thylpolysiloxane resins with the addition of TiO_2 as a colorant. The grey coating also consists of a fenylme-thylpolysiloxane resin with TiO_2 and aluminum silicate as a colorant.

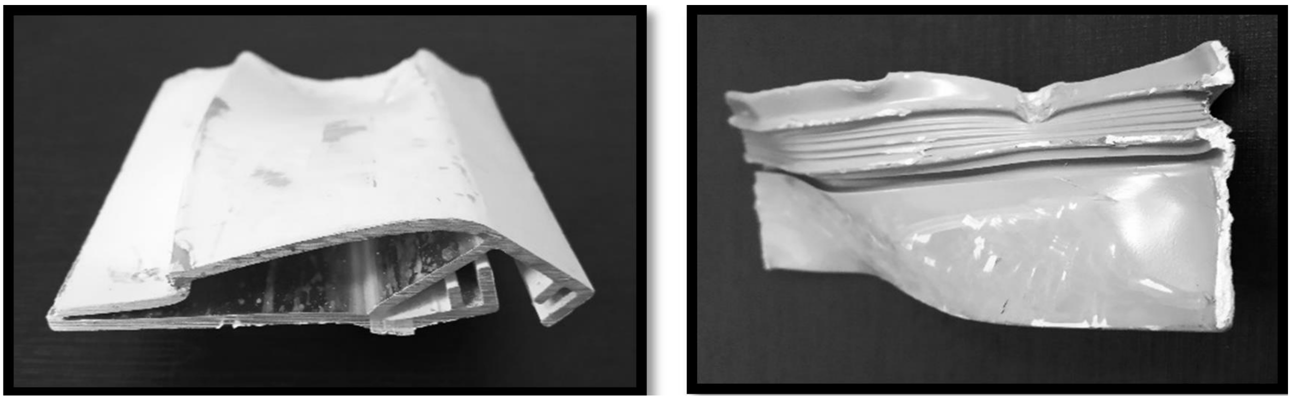

Fig. 1 *Original samples of aluminum scrap with coatings before its separation*

2.1 FTIR analysis

FTIR analysis was performed with samples of coatings divided into 7 parts and each part was exposed to a different temperature in a laboratory furnace under an air atmos-phere. The temperature range was laboratory temperature up to 650 °C, with an increasing step of 100 °C. The final temperature 650 °C was chosen according to the melting point of aluminum. After heating, the samples were ground in an agate mortar. A KBr tablet (100 mg KBr + 1.5 mg sample) was prepared from each portion of the sample and the prepared tablets were analyzed by FT-IR Nicolet 380 (Thermo Electron corp., USA) and processed using software Omnic. FTIR spectra were collected in the wavenumbers range 400 4000 cm^{-1}.

2.2 TGA analysis

The thermal stability of the coatings was also tested by TGA. TGA analysis was performed with two different samples of coatings, the sample preparation was the same as for FT-IR analysis. Approximately 20 mg of the ground samples were weighted into an alumina crucible. TGA analyzes were performed using TA Discovery TGA (TA Instruments, USA). The analysis was performed continuously in the temperature range 50 °C – 650 °C, under an air atmosphere (air flow 10 $l{\cdot}min^{-1}$).

3 Results and discussion

In this work, a study of thermal stability of organic coating was performed. Real samples of hybrid coatings, which are commonly used for surface treatment of aluminum were chosen. FTIR and TGA analysis were used for thermal stability testing of real coatings for aluminum. The samples were analyzed by continuous TGA analysis to study the behavior of the coating with increasing temperature. The structural changes of the coatings resulting from exposure of the coating to high temperature were also characterized by FTIR.

3.1 TGA analysis

TGA analysis was performed in the temperature range 50-650 °C, measurements were performed under air atmosphere. The oxidizing atmosphere simulates real conditions in the production of secondary aluminum. The results of the TGA analysis for both samples are shown in figures 2 and 3.

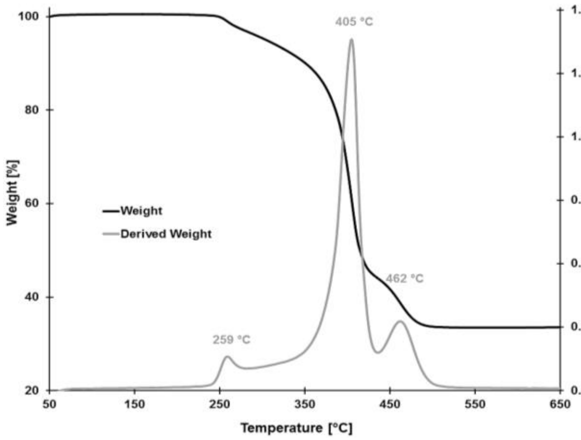

Fig. 2 TGA curves for sample of white coating

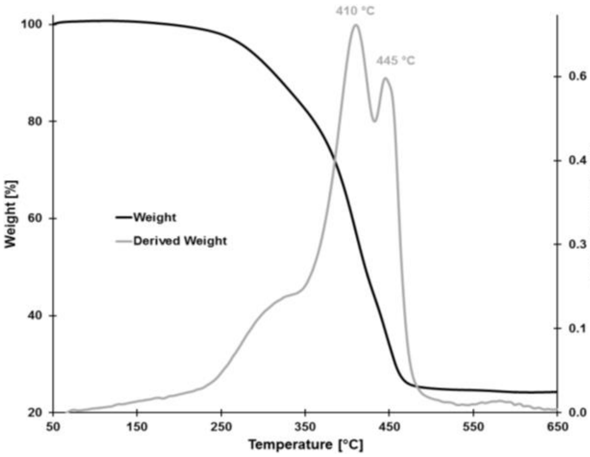

Fig. 3 TGA curves for sample of gray coating

The mass loss curve shows that the mass loss starts for both coatings at a similar temperature, approx. 150 °C. Significant mass loss is observed at a temperature range 240 – 475 °C, the remaining mass after exposure to 500 °C is approx. 25 % and 35 % respectively. With increasing temperature, the mass remains stable and no mass loss was observed. The derivation curve shows, that the mass losses of both coatings are not continuous, but there are several maxima. The derivation curve of the white coating sample shows 3 maxima, two maxima are at 259 °C and 462 °C, the highest maxima is at temperature 405 °C. The sample of the gray coating shows a gradual loss of mass in the temperature range 250 – 350 °C, which passes into two maxima at a temperature of 410 °C and 445 °C respectively. The maxima on the derivation curve correspond to the increased emissions of organic compounds and gases produced from these compounds by the degradation process.

3.2 FTIR analysis

FTIR analysis helps to study the decomposition of mainly organic groups and to confirm the production of new groups formed by oxidation and decomposition of organic compounds present in coatings. Figures 4 and 5 show the FTIR spectra for the tested coatings. Each figure shows the spectra that correspond to the coating exposed to different temperatures (laboratory temperature - 650 °C).

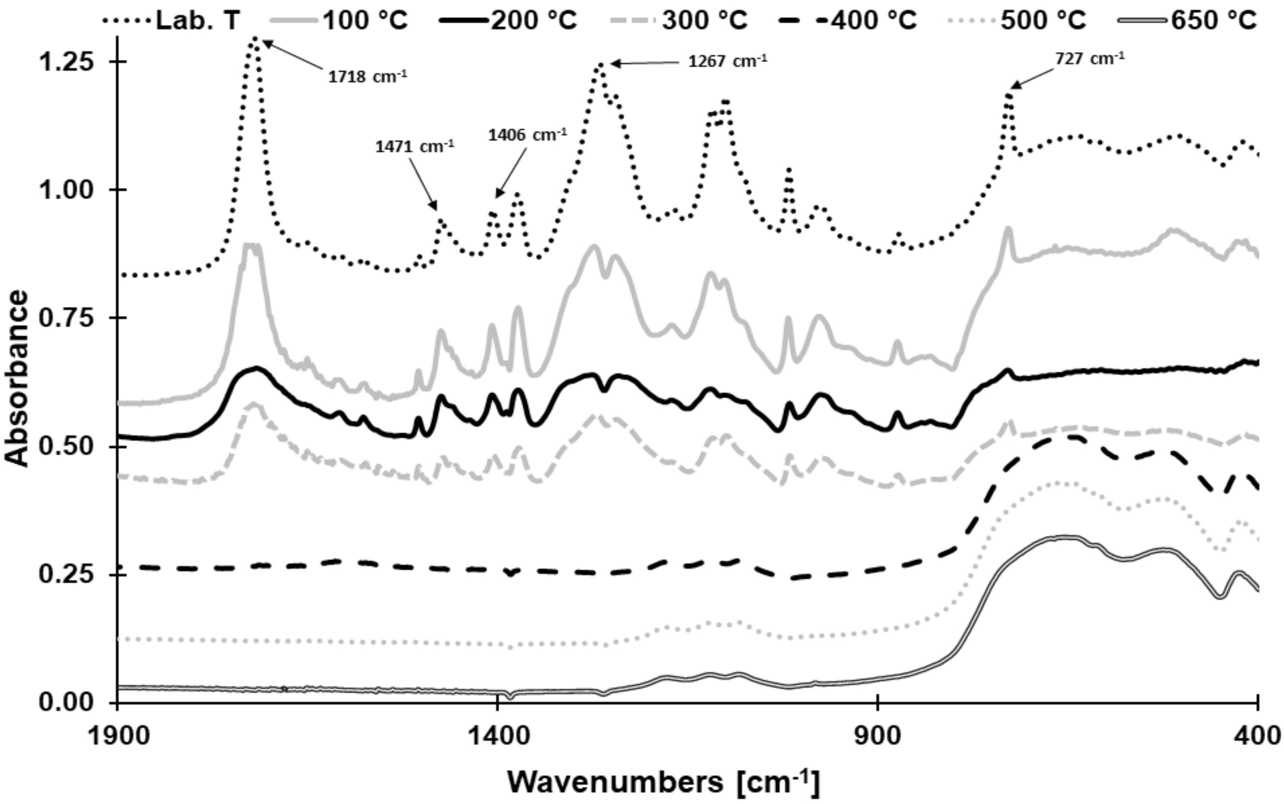

Fig. 4 FTIR spectra for sample of white coating

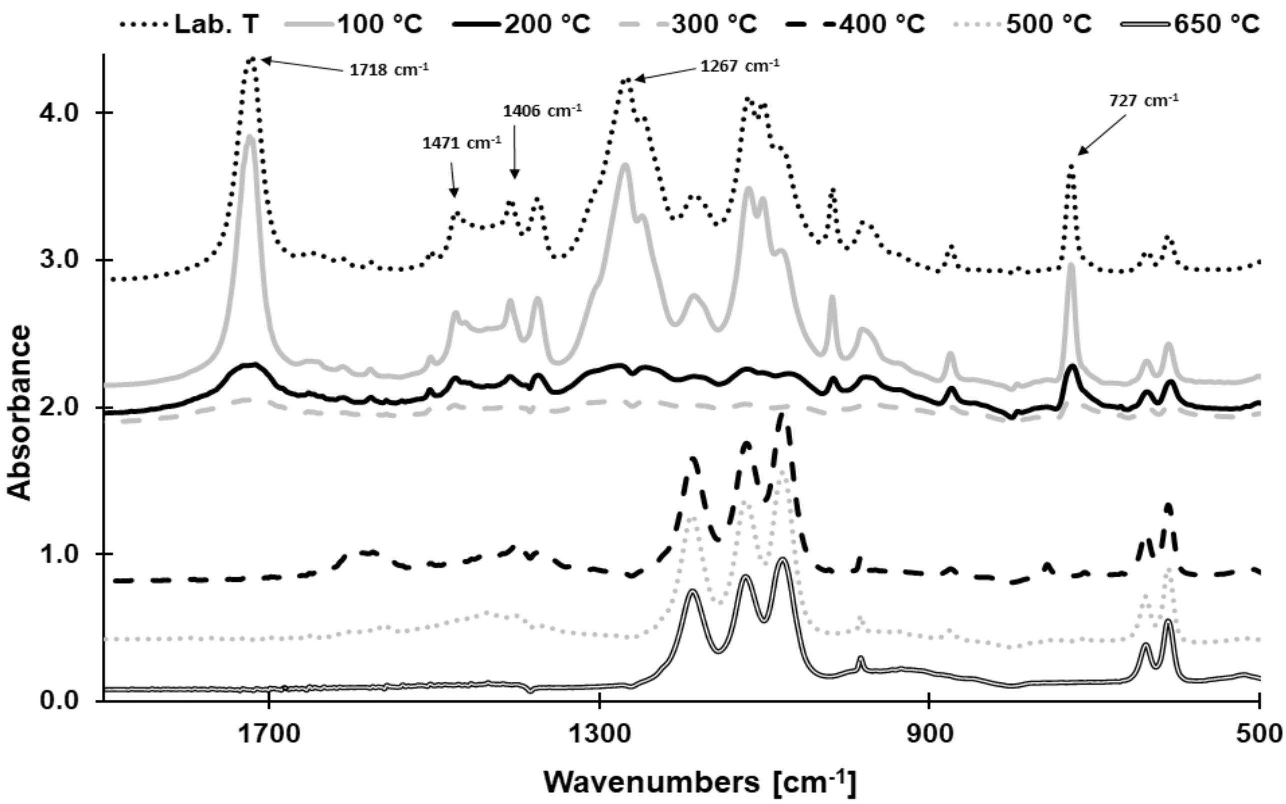

Fig. 5 *FTIR spectra for sample of gray coating*

It can be seen from Figures that a large number of peaks corresponding to different organic groups occur up to 300 °C in the FTIR spectra. The FTIR spectra of both coatings, which were not exposed to temperatures above 300 °C, are more complex than the FTIR spectra of coatings exposed to higher temperatures. The main peaks in these spectra correspond to different organic groups. The peak with wavenumbers 1718 cm^{-1} corresponds to the group C=O, wavenumbers 727 cm^{-1} belongs to methyl rocking vibration, wavenumbers 1471 cm^{-1} and 1267 cm^{-1} belong to bond C-H and wavenumber 1406 cm^{-1} corresponds to COOH group. Spectra of samples exposed to higher temperature (above 300 °C) are simple and most of peaks presented in the spectra at lower temperatures disappear. Spectra of white coating sample are without visible peaks. From spectra of gray coating disappear most of peaks that correspond to various organic groups, on the other side is apparent that some new peaks appear, especially at wavenumbers region 950-1200 cm^{-1}. These peaks correspond to inorganic bonds of Si-O and Si-O-Si group. New peaks corresponding to inorganic rest of the coatings. Inorganic part is presented even at lower temperature, but peaks are overlapped by dominant peaks of organic groups. Presented organic compounds are decomposed after exposure to higher temperature and they are removed from coatings as an emitted gas. Most of remaining coating mass are made up of original inorganic part and of inorganic constituent formed as a results of high temperature exposure.

Results obtained by FTIR complement and confirm results obtained by TGA analysis. Both methods prove that tested coatings are not thermally stabile and if are exposed to temperature above 300 °C, degradation of organic part begin. Coatings degradation proceeds in narrow range of temperature and in samples exposed to temperature above 450 °C are degradation of organic part finished and rest only inorganic part remain.

Thermal stability have a key role during process of aluminum recycling. Most of coatings must be removed from aluminum scrap before recycling. Coatings or it`s rests caused various problems during production of secondary aluminum. In case of high thermal stability of coatings, rests of coatings influenced final quality and properties of produced secondary aluminum. In contrast, low thermal stability of coatings can caused emission of various toxic compounds from coatings and/or production of toxic products of degradation.

4 Conclusion

The results obtained by TGA analysis are in a good agreement with results obtained by FTIR. Both methods confirmed degradation of organic coatings with increasing temperature. Degradation of the organic coatings begins at temperature less than 150 °C and is completed at 500 °C, farther increasing of temperature is not accompanied by mass loss.

Approximately about 25 % of coating mass is thermostable (pigments and other inorganic compounds presented in organic coatings).

Presented results shows that the tested coatings have low thermal stability, on the other hand, low thermal stability cannot be utilized in process of aluminum recycling. Tested hybrid coatings contain thermostable inorganic part which can affect quality of produced secondary aluminum. During processing of coated aluminum scrap attention must be paid to decomposition of organic compounds and production of toxic gases, which can affect the human health. Large quantities of processed aluminum scrap lead to the emission of toxic gases into the atmosphere and contribute to environmental pollution.

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