Study on pyrolysis behavior of polymeric coated aluminium scrap using TGA and Py-GC/MS

Vichaphund S., Wimuktiwan P., Soongprasit C., Soongprasit K., Phetchcrai S., Sirichaivetkul R., Atong D.

National Metal and Materials Technology Center, National Science and Technology Development Agency, Pathumthani, Thailand

Abstract

The polymeric coated aluminium scrap obtained from local recycling plant in Thailand was used as a raw material. The thermal decomposition behavior and evolved gas from pyrolysis of polymeric fraction coated on the aluminium surface was investigated using thermogravimetric analysis (TGA) and pyrolysis-GC/MS (Py-GC/MS). Initially, thermogravimetric analysis (TGA) was used to study the thermal decomposition of all coated aluminium scrap (white, black, and brown color). From TGA results, a major thermal degradation at 300-480°C associated to the decomposition of polymeric fraction was found in all powder coating samples. The weight loss was 5.03 wt%, 4.08wt% and 1.49 wt% for the white-coated, black-coated, and brown-coated scrap, respectively. Then, the pyrolysis of polymeric layer coated on aluminium surface was investigated using a Py-GC/MS. The effect of pyrolysis temperature (400-600°C) and types of coated aluminium scrap on the product selectivity was studied. In term of pyrolysis, the polymeric materials used in the coating would decompose via scission reaction generating volatile compounds. At temperature of 600°C, the pyrolysis vapors from white-coated scrap contained a high proportion of ester (45.11%) and carboxylic acid (37.49%) with small amount of aliphatic HC (7.80%) and aromatic HC (1.11%). On the other hand, the volatile decomposed from other samples showed high proportion of esters (46.07%-55.97%) and hydrocarbons (16.71%-24.61%). Aliphatic hydrocarbon consisted of alkenes, alkynes and cycloalkenes, while aromatic hydrocarbons were C_7-C_{12} composed of toluene, biphenyl, styrene, etc. In addition, the low fraction of N-containing compounds (5.90%-6.58%) from the decomposition of cross-link agent were found in all coated samples.

Introduction

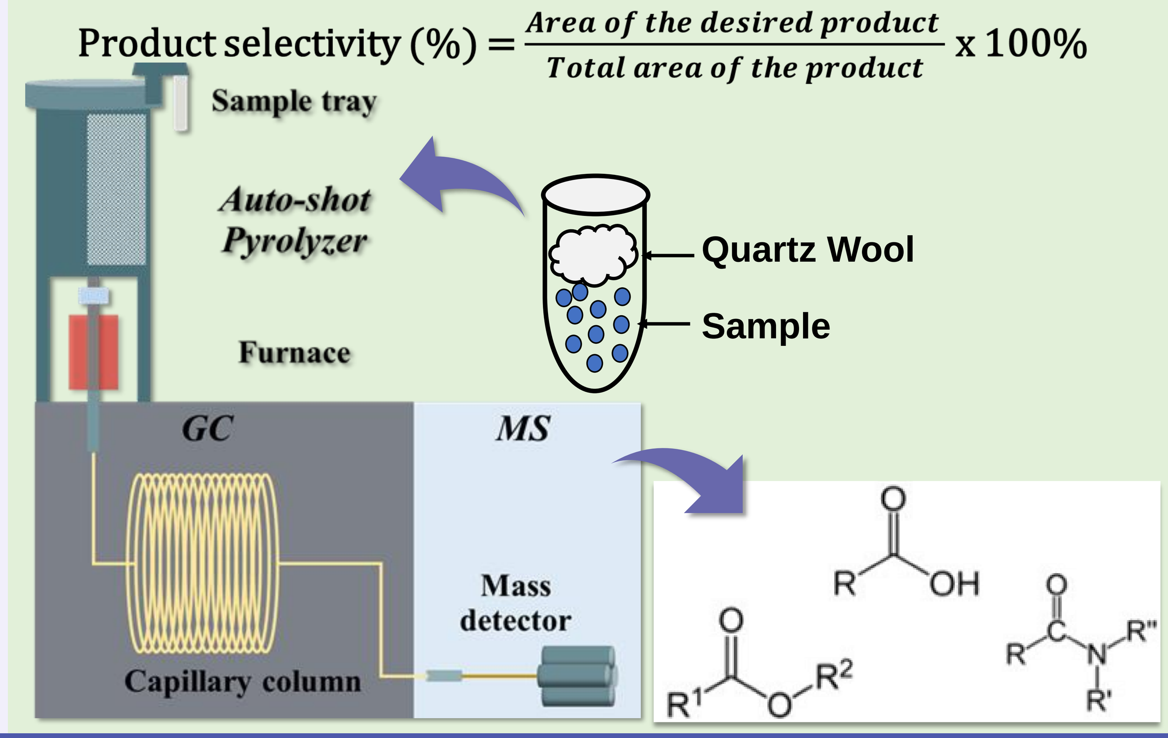
Aluminium recycling has significant positive impacts on the economy and environment because the process requires only 5% of the energy used to produce primary aluminium. In 2020, annual global demand for aluminium reached to 97 million tons, of which more than 30 million tons is expected to be supplied from scrap recycling. Recently, aluminium is coated with organic compounds such as polyesters and epoxy resin to enhance corrosion resistance while promote fine appearance at the same time. Coated aluminium has been widely used in several applications such as transportation, packaging, electronics, and construction. During recycle process, direct re-melting of coated scrap causes large amount of gas emission which reduces the quality and quantity of metal. Thus, the removal of polymeric coating by heat treatment (thermal-decoating) prior to re-melting should be applied to mitigate the aforementioned problem. Pyrolysis is the most promising technique to investigate the degradation behaviour of powder coating which would provide insightful information for further optimizing the de-coating process of aluminium scrap.

Objective: The polymeric coated aluminium scrap from local recycling plant was pyrolyzed and monitored thermal behavior of coating materials in terms of the mass loss, evolved gases, and residues after thermal treatment (de-coating) in order to obtain useful information for improving the aluminum recycling process.

Methods

Aluminium window frames

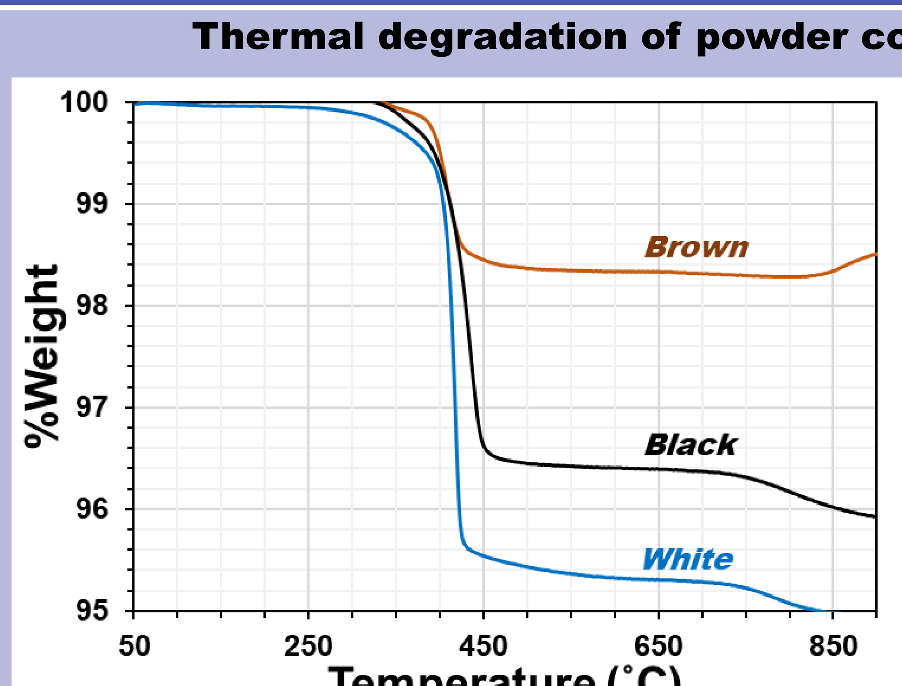
$$\text{Product selectivity (\%)} = \frac{\text{Area of the desired product}}{\text{Total area of the product}} \times 100\%$$

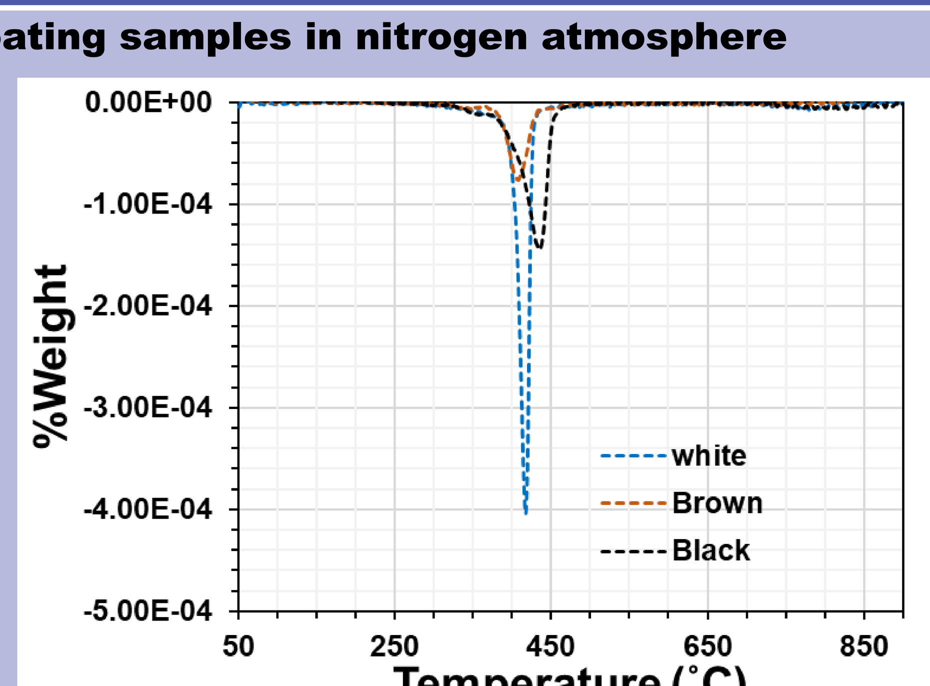


Parameter	Condition
Pyrolyzer (PY)	
Temperature (˚C)	400 500 600
Pyrolysis time (sec)	30
Carrier gas	He, 5 mL/min
Injection temperature (˚C)	280
Gas Chromatography (GC)	
Capillary Column	Ultra alloy -5 (UA-5)
Temperature	50 ˚C, 3 min 50-200˚C, 5˚C/min 200-350˚C, 10˚C/min 350˚C, 10 min
Carrier gas	He, 5 mL/min
Mass spectrometer (MS)	
m/z (70 eV)	20-800
Scan time (s)	0.2
Scan rate (amu/s)	625

Results-Discussions

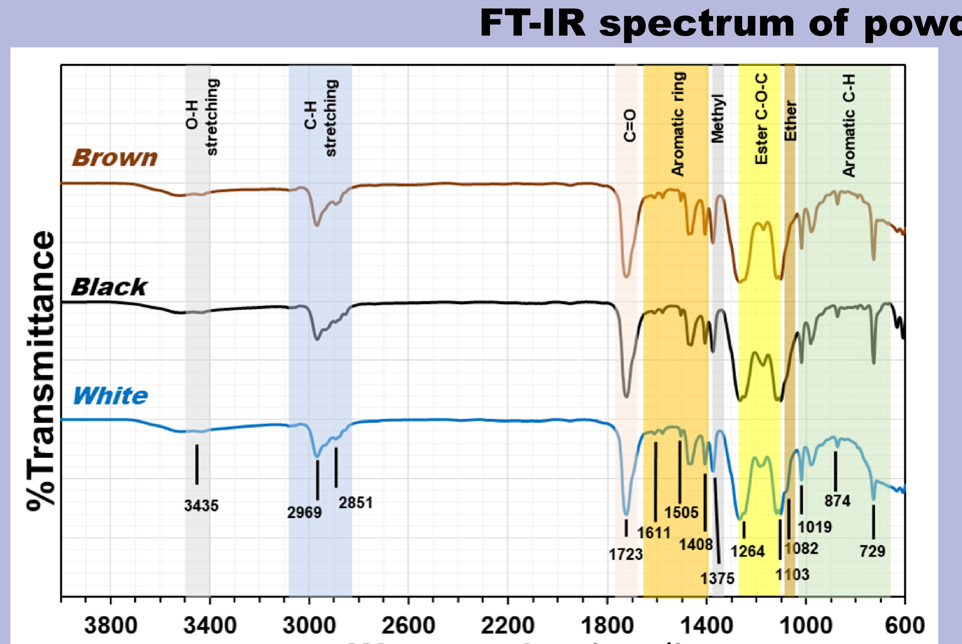
Thermal degradation of powder coating samples in nitrogen atmosphere





A major thermal degradation of all powder coating samples was occurred at 300-480°C associated to the decomposition of polymeric fraction. The weight loss for the white-coated, black-coated, and brown-coated scrap were 5.03 wt%, 4.08wt% and 1.49 wt%, respectively

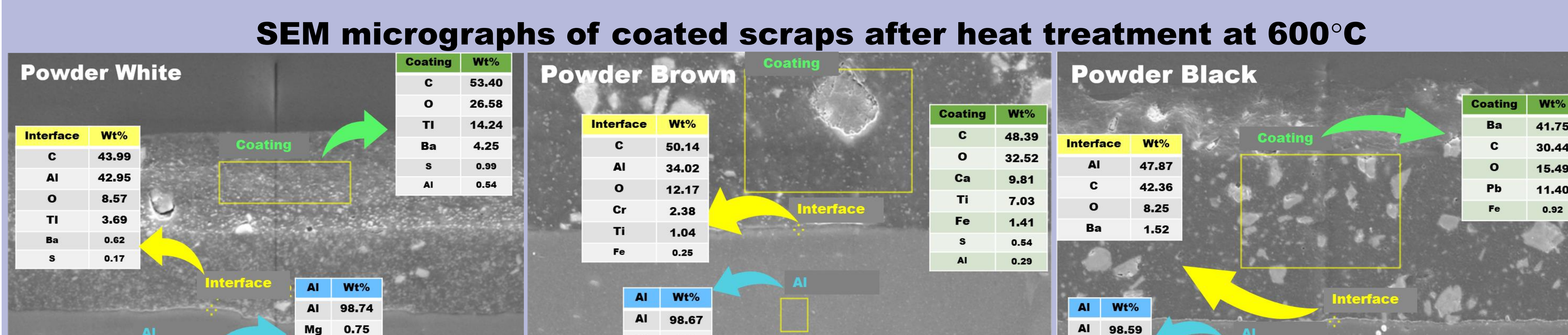
FT-IR spectrum of powder coating samples



Signal peak (cm^{-1})	Assignment
3435	O-H stretching (Aromatic)
2851-2969	C-H stretching (Aliphatic)
1723	C=O stretching (Ester carbonyl)
1611, 1505, 1408	C-C stretching (Aromatic)
1375	methyl
1264, 1103	C-O-C (Ester)
1083	Ether
1019, 874, 729	C-H bending (Aromatic)

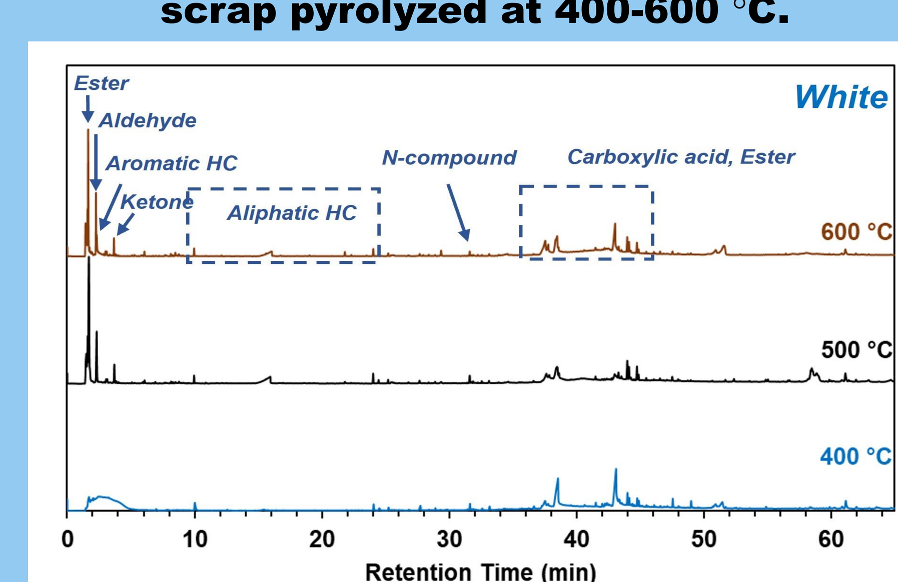
The chemical compositions were mainly composed of compounds with C-H, C=O, aromatic ring, methyl and aromatic bonds, indicating that these organic coating materials was polyester compound.

SEM micrographs of coated scraps after heat treatment at 600°C

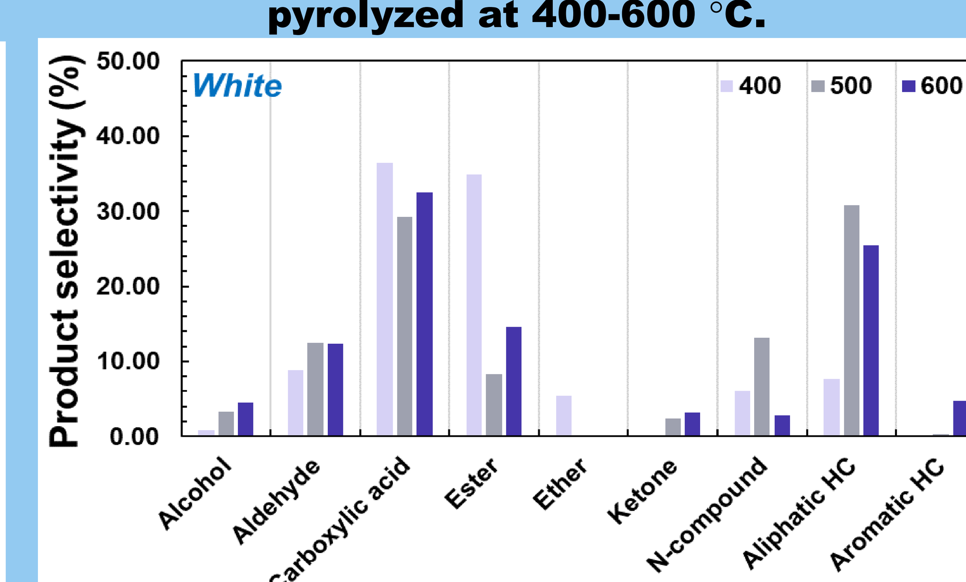


After heat treatment at 600°C, the ash composition was determined by EDX technique. The main compositions of white-ash and brown-ash were C, O, Ti and Ca, while the element of black-ash consisted of Ba, C, O and Pb, respectively. The nonvolatile fraction at the end of heat treatment was chiefly associated to TiO_2, CaO as the pigment component, and also $BaSO_4$ as a filler for formulating the pigment for powder coating process.

The GC/MS chromatograms of white-coated scrap pyrolyzed at 400-600 °C.

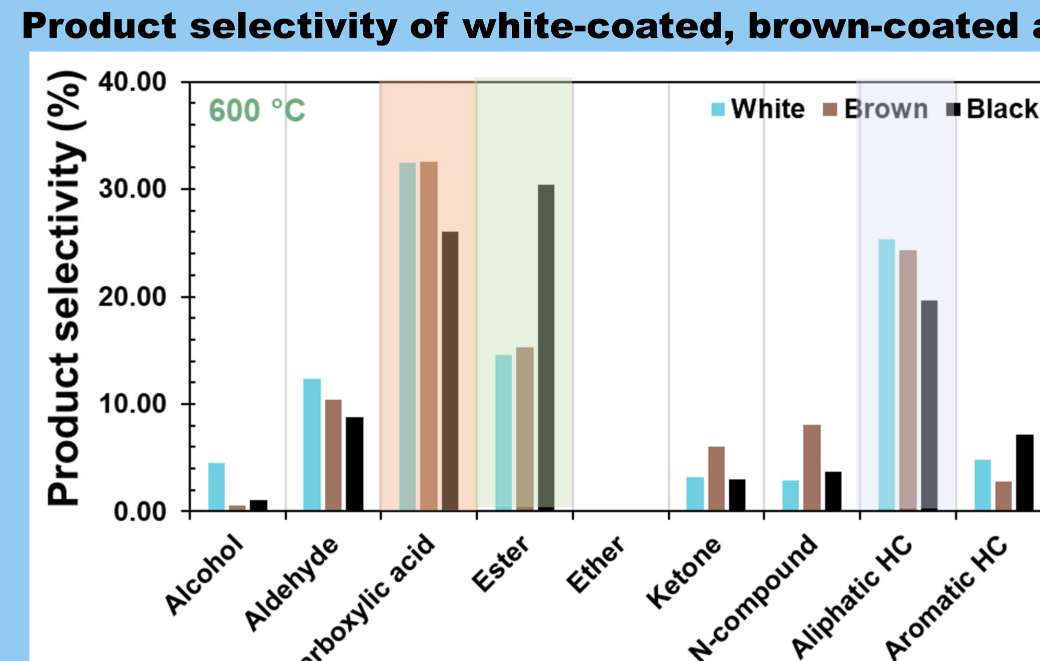


Product selectivity of white-coated scrap pyrolyzed at 400-600 °C.



At low RT, the low molecular species are detected such as alkene, aldehyde, ketone, ester and aromatic compounds, whereas the higher MW compounds including carboxylic acids (C_{13}-C_{18}) and esters (C_{12}-C_{18}) were found at RT in range of 31-45 min. These compounds are produced by both β-and α-hydrogen bond scission. The maximum temperature (600 °C) promoted high yield of hydrocarbons (aromatics and aliphatics) from robust scission, cracking and deoxygenation reactions.

Product selectivity of white-coated, brown-coated and black coated scrap pyrolyzed at 600 °C.



The pyrolysis vapors of white-coated scrap contained a high proportion of ester (14.60%) and carboxylic acid (32.48%) with small amount of aliphatic HC (25.34%) and aromatic HC (4.82%).

The volatile decomposed from brown and black coated samples showed high proportion of esters (15.27-30.43%) and hydrocarbons (19.69%-24.30%).

Aliphatic hydrocarbon consisted of alkenes, alkynes and cycloalkenes, while aromatic hydrocarbons were C_7-C_{12} such as toluene, biphenyl, styrene, etc. In addition, the low fraction of N-containing compounds (2.84%-8.08%) from the decomposition of cross-link agent were found in all coated samples.

Conclusion

The highest pyrolysis temperature of 600°C was the optimum condition for removal of the polymeric layer by generating the largest proportion of evolved gases from coated aluminium materials. Obtained data would provide useful information for improving the aluminum recycling process such as controlling organic evolved gases, process optimization as well as feasible design for thermal-decoating and remelting furnace.

The authors gratefully acknowledgments the Program Management Unit-Competitiveness : PMU-C, CAP Global Aluminium Co., LTd. and National Metal and Materials Technology Center (MTEC:P2151462) for the financial support and providing the samples.