Heavy metals in plastic, recycling and environmental aspects

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■ Overview

Plastic has become an integral part of our daily life and it's use is increasing. In 2013 the worldwide production has reached an all-time high of about 300 million tons (MT). Single use-packaging accounts for almost 40%, of the total production.

In the past the Life Cycle Assessment (LCA) was linear, after usage it turned into waste and ended meanly as landfill. Under consumer and political pressure the EU presented a green paper in 2013[1] indicating that it has to become a circular economy. In these economical tough times recycling could create about 160.000 jobs if the recycling rate goes up to 70% in 2020.

Is recycling of single use material easy? Modern packaging materials consists of several layers, each layer has special properties. By physical recycling these properties are lost and recyclates are becoming a complex mixture.

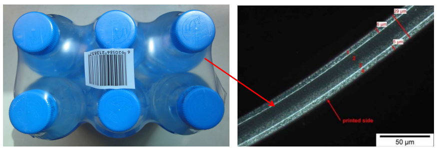

Figure 1 and 2: For instance modern shrink films: films are 30 µm thick and can consist out of four (or more) layers.

■ Heavy metals in modern plastics

Due to regulation toxic heavy metals are regulated by law, e.g. REACh, EG 1907/2006, and RoHS, 2011/65/EU. For instance cadmium and lead are regulated, resp. max. 100 and 1000 ppm.

In the past these restricted metals where only used as stabilizer and/or colorant. Nowadays restricted metals back are found in food packaging as catalyst leftovers of catalyst of polymerization (monomers are becoming plastic).

For instance PET (PolyEthylene Terephthalate) is a widely used material in food-packaging. The polymerization of PET is catalysed with antimony-compounds. Antimony can leak (migration) out of polymer matrix into the beverage.

PET is the succes story of the recycling industry. Taxes on PET-bottles in the western world produces a clean raw material. In the 2nd and 3th world is recycling of PET waste to raw material is profitable.

Figure 3 and 4: Sorting of grinded PET bottles on impurities in Pakistan.

The catalyst antimony in PET is restricted in tapwater: 5 µg/L (WHO). PET is nowadays used in several daily apllications. Even in tea bags.

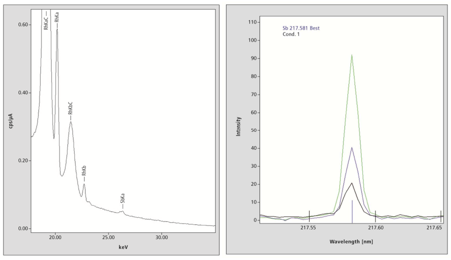

Figure 5: Extract from an EDXRF spectrum showing Rh and Sb lines. The Rh lines are created by the X-ray tube (Rh target). Figure 6: Emission profile of antimony generated by ICP-OES technique. Blue: 5 µg/l Sb, green: 10 µg/l Sb and a five-fold dilution of tea prepared with the fine structured PET bag (black).

A tea bag made of very fine structured PET was further examined. After 5 minute brew process the sample released the highest amount of antimony in the water: 8.4 ± 0.8 µg/l. This is significantly above the maximum concentration defined by Council directive 98/83/EC.

■ Inheritance of the past

Recycling of plastics from durable application, e.g. cars, electronics or crates, is becoming increasingly complex. During their functional life the meantime new regulations were introduced. For instance RoHS (2011/65) restricts the maximum concentration of toxic metals in electronic applications.

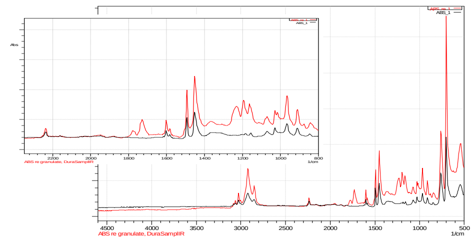

Figure 7: FTIR-ATR absorption spectrum of virgin ABS (black) and recycled post-consumer ABS from electronics (red)

The additional peaks in the red FTIR-ATR spectrum are the result of contamination and are not recognized by traditional libraries.

Analysis with the EDXRF gives more information of the elements present in the plastic. The presence of bromine and synergist antimony shows that the recycled ABS contains low concentrations of bromated flame retardants. Furthermore highly toxic cadmium is detected.

Element	Virgin ABS [mg/Kg]	Recycled ABS [mg/Kg]	Possible function
Cl	-	357	Flame retardant
Br	-	1985	Flame retardant
Sb	-	1356	Synergist flame retardant
Ba	-	209	Filler
S	120	660	Production, Filler component
Cd	-	257	Stabilizer

Table 1: Results of X-ray screening and RoHS analysis of virgin and recycled ABS

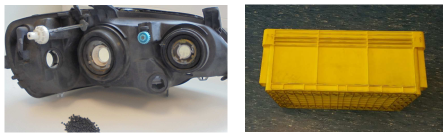

Figure 8 and 9 Typical examples of durable plastics that nowadays are recycled: automotive parts and crates.

EDXRF analysis: in the black automotive parts lead was detected : 1124 ppm whereas the yellow crates contain Cd : 2016 ppm.

■ Plastics in the environment

Plastics are organic substances (carbon-backbone) which are sensitive for degradation. As a result of e.g. UV-radiation, the carbon-backbone will be broken and oxygen is adopted. Hereby mechanical stability is reduced and plastic deposits in the oceans are grinded down by waves: plastic fragments are formed .

Nowadays plastic fragments are found back in the food chain. Since decennia IMARES conducts research on the stomach content of dead beached fulmars.

Figure 10 and 11 Dissection of beached dead fulmars. Plastic is found back in the stomachs (proventriculus and gizzard).

With EDX-RF it is possible to screen the plastic fragments on presence of nowadays forbidden heavy metals. The technique is, like FTIR-ATR, non-destructive. After calibration it is possible to quantify the elements like Cd, Pb, Hg, Cr and Br (which are restricted by RoHS directive 2011/65 and REACh directive 1907/2006).

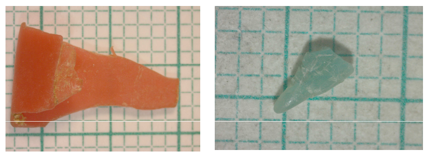

Figure 12 and 13 Plastic fragments found back in the gizzard of fulmars.

The read/orange plastic fragment contains 2171 ppm Cd and the blue fragment 130 ppm Pb.

■ Conclusion

Heavy metals like Pb or Cd will negatively influence the reuse of the man-made material and therefore is a source of pollution. More analytical efforts are necessary to describe the possible recycling application of plastic waste.

■ References

[1] EU Green paper, On a European Strategy on Plastic waste in the Environment http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:52013DC0123&from=EN

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