



# 32th European Congress on Molecular Spectroscopy 2014

Bar  
Café  
Bistro



EUCMOS 2014 Düsseldorf

24.8.2014 – 29.8.2014

Heinrich-Heine-Universität Düsseldorf

## Book of Abstracts

Editor: Michael Schmitt

ISBN: 978-3-00-046327-3

Session 3: Environmental Applications in Spectroscopy  
EAS 3.1 Monitoring Plastic Waste Using FTIR Spectroscopy

Albert van Oyen<sup>a</sup>, Jan Andries van Franeker<sup>b</sup>, Uwe Oppermann<sup>c</sup>, Marion Egelkraut-Holtus<sup>c</sup>

<sup>a</sup> *Research, Harderhook 20, D-1432 Bocholt, CARAT GmbH, Germany*

<sup>b</sup> *Research, PO Box 167, 1790 AD Den Burg Texel, IMARES, Netherlands*

<sup>c</sup> *Spectroscopy, Albert- Hahn- Str. 6-10, D-47269 Duisburg, Shimadzu Europa GmbH*

The production of plastic has reached an all-time high, for instance in 2012 there has been 288 million ton (MT) produced worldwide[1]. According to the United Nations Environment Program it is estimated that annually 6.4 Mt plastic ends in our seas and oceans worldwide. Estimates of the total volume in our oceans exceed more than 100 Mt [2] but more and more research assumes this is an underestimation.

In the environment degradation of plastic takes place. Under influence of UV-radiation and the ocean waves, big pieces of plastic are grinded into microplastics (< 5 mm). A large amount of these plastics will wash up the beaches where the sand is abrasive. The sand stores a lot of heat and exchanges this with the plastics, which accelerates the degradation.

An FTIR spectrum of a Polyethylene (PE) fragment in the environment differs strongly from the virgin state of PE as it was produced. The result of degradation are lot of new peaks. At this time, it's a well adopted opinion that degradation of PE mainly takes place on the surface. The plastic fragments on beaches getting sanded and small pieces released of the surface, are forming an invisible pollution. The plastic soup is becoming a plastic bouillon. Experimental work is in progress for analyzing the micro particles.

Marine biota mistakes plastic for food. Well known are the pictures of Chris Jordan [3] of albatross chicks which died of hunger but having a stomach full of plastics. Nowadays more and more researches are concentrating on the stomach content of fish and birds. About 95% of the North sea fulmars have plastic in their stomach. In the 1980s about half of these ingested plastic were industrial pellets, but nowadays 80% by mass is consumer waste, mostly PE.

For interpretation of FTIR spectra currently the majority of the polymer- or plastic libraries are using spectra of prime materials and are very useful for prime materials, polymer production waste, pre-consumer recyclates but insufficient for post consumers recyclates and plastic found in the environment.

Plastics are not inert but change over time as they are thermodynamically metastable. Plastics are losing their preferred and desired mechanical and thermal properties. Therefor the plastic recycle market is limited by the thermo dynamical state of the wasted plastics. The identification of plastic in our environment needs an updated determining method.

FTIR-ATR is a strong tool for identifying plastic over a long period of time, or even better over a degradation period. With the right library, FTIR-ATR is a helpful tool for polymer industry as well as for pre- and post- consumer plastic waste recycler, and for the researchers who are describing the plastic waste in our environment.

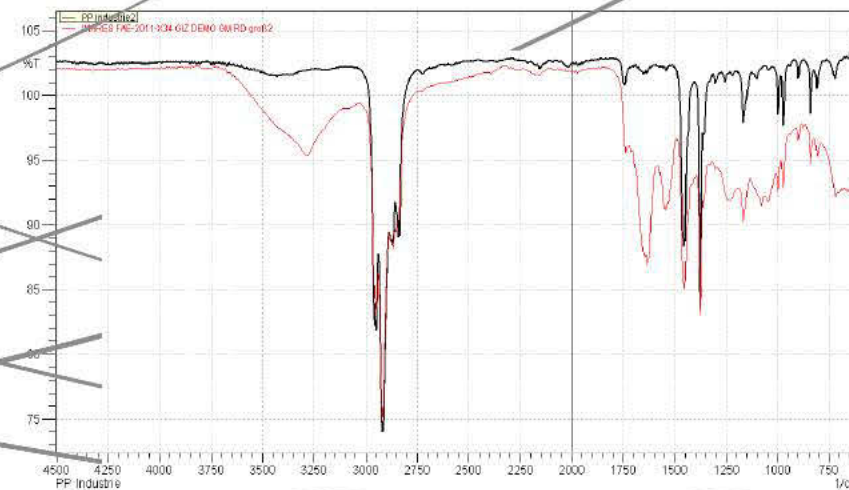
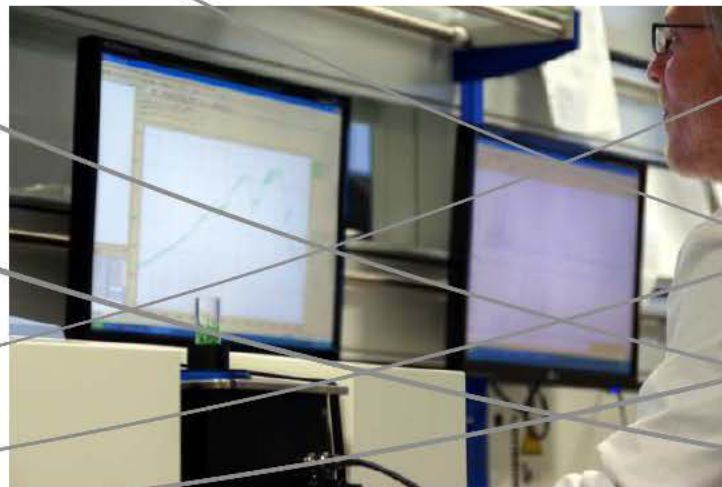
*Keywords: FTIR-ATR Spectroscopy; Plastic; Environment, Wildlife*

## References

- [1] Plastic the facts 2013, <http://www.plasticseurope.org/Document/plastics-the-facts-2013.aspx?FolID=2>
- [2] UNEP, year book 2012, <http://www.unep.org/yearbook/2012/>
- [3] Midway: Message from the Gyre, <http://www.chrisjordan.com/gallery/midway/>
- [4] IMARES, Wageningen UR, Plastic waste in the Sea, [www.wageningenur.nl/plastics-fulmars](http://www.wageningenur.nl/plastics-fulmars)



# Monitoring Plastic Waste using FTIR-ATR Spectroscopy





# Monitoring Plastic Waste using FTIR-ATR Spectroscopy

- Plastic a man-made material
- CARAT
- Short introduction to plastics
  - Additives
  - Waste
  - Recycling, the solution?
  - Degradation
  - Post consumer plastic
- Plastic a BIG environmental problem
  - Beached
  - Eaten
  - Biofouling
- Summary





# Plastic: a man-made material

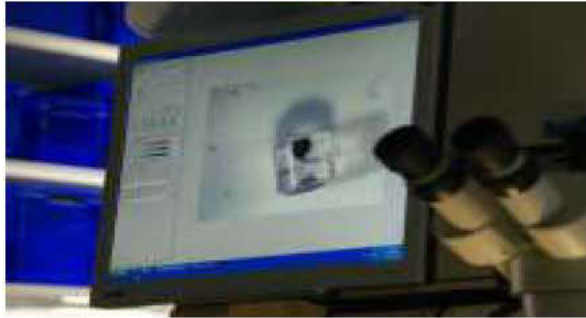
Plastic production is all time high. The use of fossile fuels as raw material and environmental issues makes the discussion of an economical very succesfull man-made material hot.





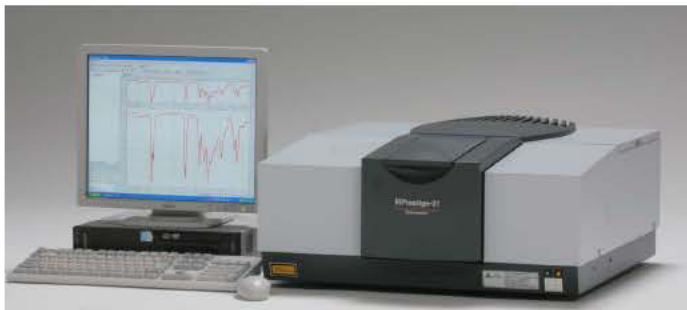
# CARAT: Control And Research Analysis Thermoplastics

Carat analyses the standard properties of plastic for the compounding and injection moulding industry: e.g. MFR, viscosity and impact strength but also element-analyses.



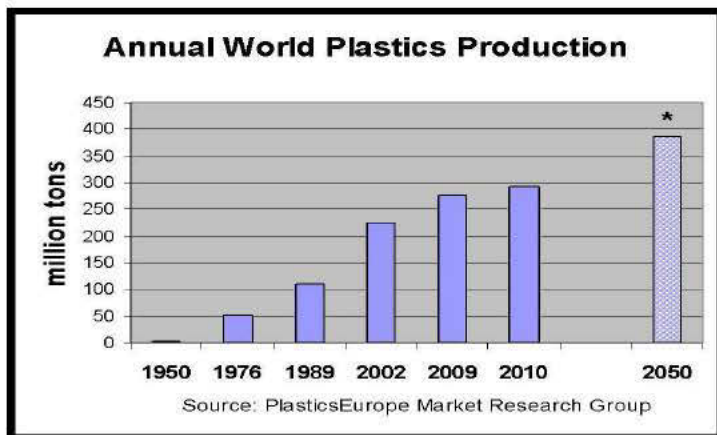
Analysing the basic properties of recycled plastic are a challenge.

Furthermore in cooperation with Shimadzu and IMARES we're trying to describe plastic waste in the environment with FTIR-ATR.



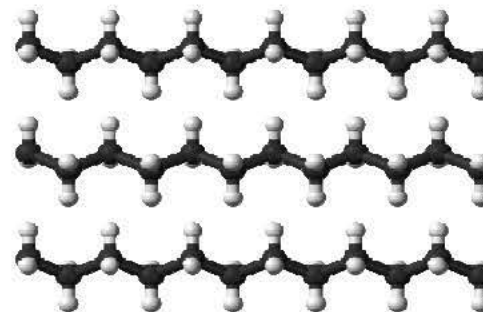
# Short introduction to plastic

In 1907 the first real plastic innovation was introduced: bakelite. In 1951 the annual production of plastics was 1,5 Mt. Figures show that in 2011 the annual production was 280 Mt. In the last decade more plastics are produced than in the whole century before.



This are mainly thermoplastics. In contrast to bakelite thermoplastics have no 3D structure (like thermosets) but a 2D structure. The long chains are more flexible and the material can be remelted: reused or recycled.

This flexibility explains the succes of plastics, especially in food packaging.







# Short introduction to plastic: additives



There are hundreds of different kinds of plastic. But to make it more complex the plastics can also possess different kinds of additives, e.g. glassfibres, minerals, colorants, UV-stabilisers and flame-retardants. Plastics can be tailor-made for the application.



For virgin and pre-consumer plastics FTIR-ATR is a quick and easy method and with the commercial libraries it is simple to classify the plastic.



# Short introduction to plastic: waste

Since the seventies plastics are more and more used in disposables, especially foodpackaging. After consuming the desired content, the packaging becomes waste and ends (partly) in the environment.



Natural disasters are also a source (Photo's tsunami Japan 2011) .





# Plastic waste: recycling the solution?



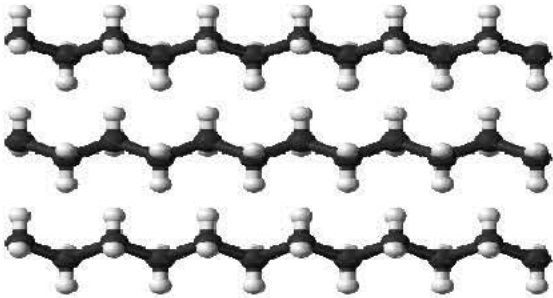
In the EU plastic-waste is a hot item, in march 2013 the EU commission presented a Greenbook. Plastic recycling, according to the EU, has the opportunity to create in Europe more than 160.000 jobs.



But is recycling so simple? Foodpackaging consist out different layers of different plastic. Recycling mixes these plastics. The wanted special properties are lost.

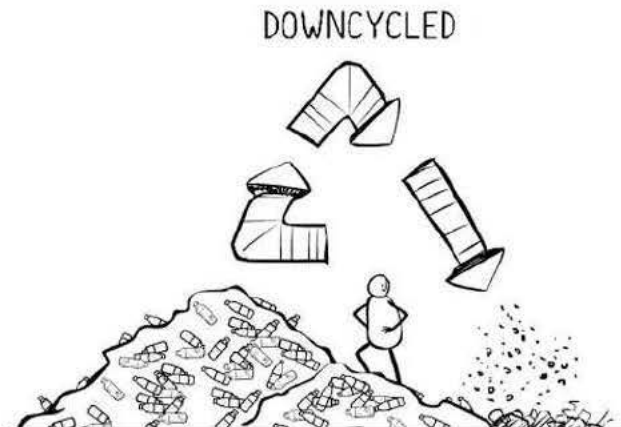
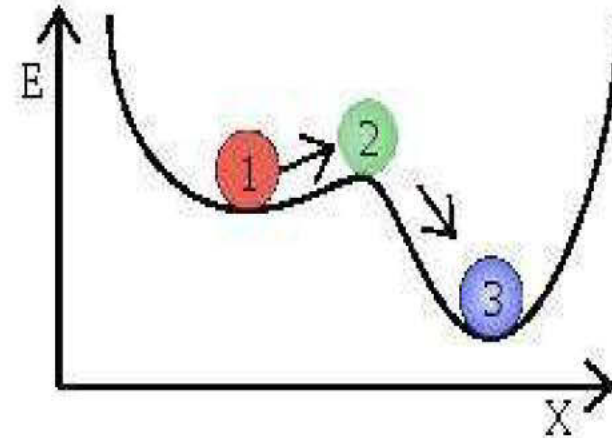


# Another recycling problem: degradation



Plastics have a carbon-backbone, this means that the material is not inert, chains will break and for instance oxygen is adopted.

Thermodynamically: plastics are meta-stable so by sufficient extra energy, eg. heat or UV-radiation, the material will degradate.



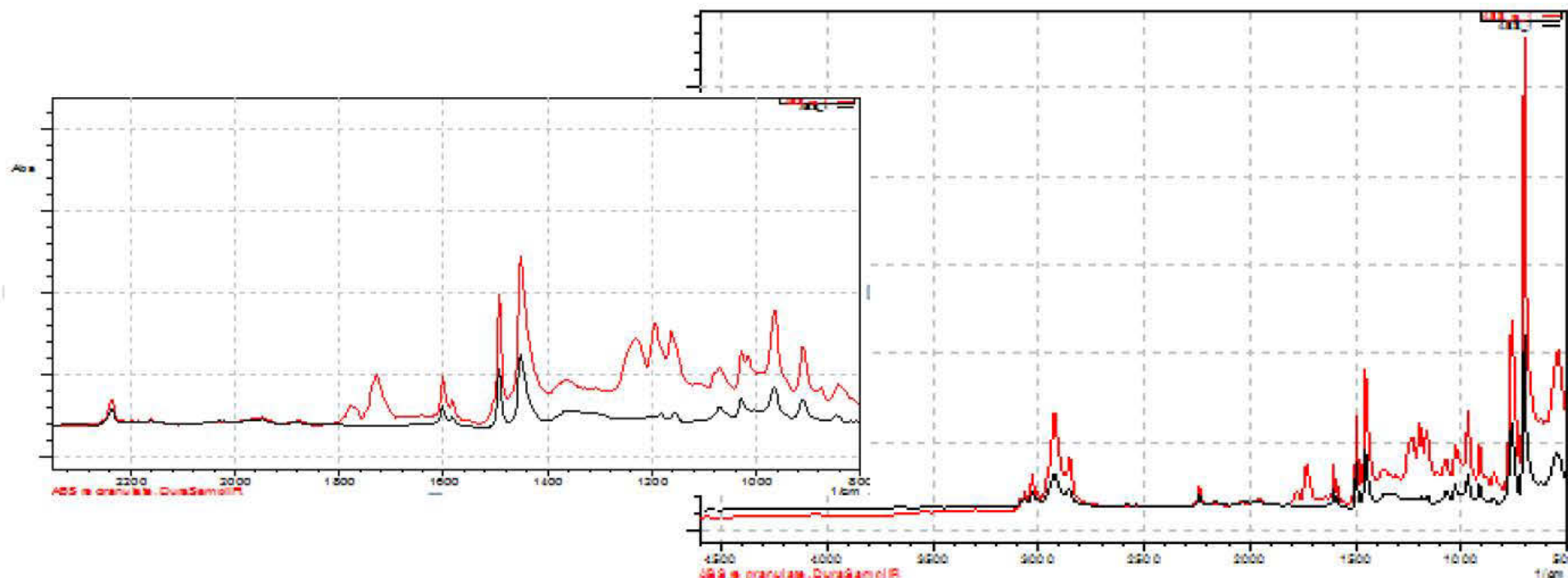
The complex composition of modern plastics makes recycling of plastics very difficult. A complex infrastructure is needed to make recycling a success.



# Recycling post-consumer plastic

Practice: recycled ABS of electronic parts (post-consumer).

FTIR-ATR: Virgin (black) vs post-consumer (red) ABS (terpolymer of acrylonitril/butadien/styrene)



FTIR Spectra of virgin and post consumer waste. Additional peaks appear, especially over the region 2000- 1000 cm<sup>-1</sup>. The material could be contaminated with polycarbonate or a brominated flame-retardant.



# Recycling post-consumer plastic

EDX RF analysis gives some extra information.

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

The material contains bromine and antimony. Antimony is used as a synergist in brominated flame-retardants. Probably the extra peaks are from a flame retardant.

Furthermore the material contains cadmium. Cd is used in the past as a stabiliser and colorant but is highly toxic.



Nowadays Cd is forbidden in many applications (RoHS and REACH) so this recyclate does not fit for reuse, an option is thermal recycling.





# Recycling post-consumer plastic

The general problems with recyclates, especially post-consumer, is the unknown history and composition of the material. For determination of applications of this material many extra costly analysis are necessary.



Summary: these extra (control) analysis make recyclates expensive (even more than virgin materials from the industry).

This is a big challenge for the EU and the (recycling-)industry to overcome.





# Plastic a BIG environmental problem



Estimations of the UNEP: annually 6.4 Mt plastic ends in our seas and oceans worldwide. Plastic in the environment is a worldwide problem. UV-Radiation changes the chemical composition of plastic, the material is getting brittle.

In rivers, seas and oceans big plastic parts are mechanically broken by waves: microplastics are generated (dimensions  $< 5$  mm). Industrial pellets, the so-called mermaid tears, are also regularly found.

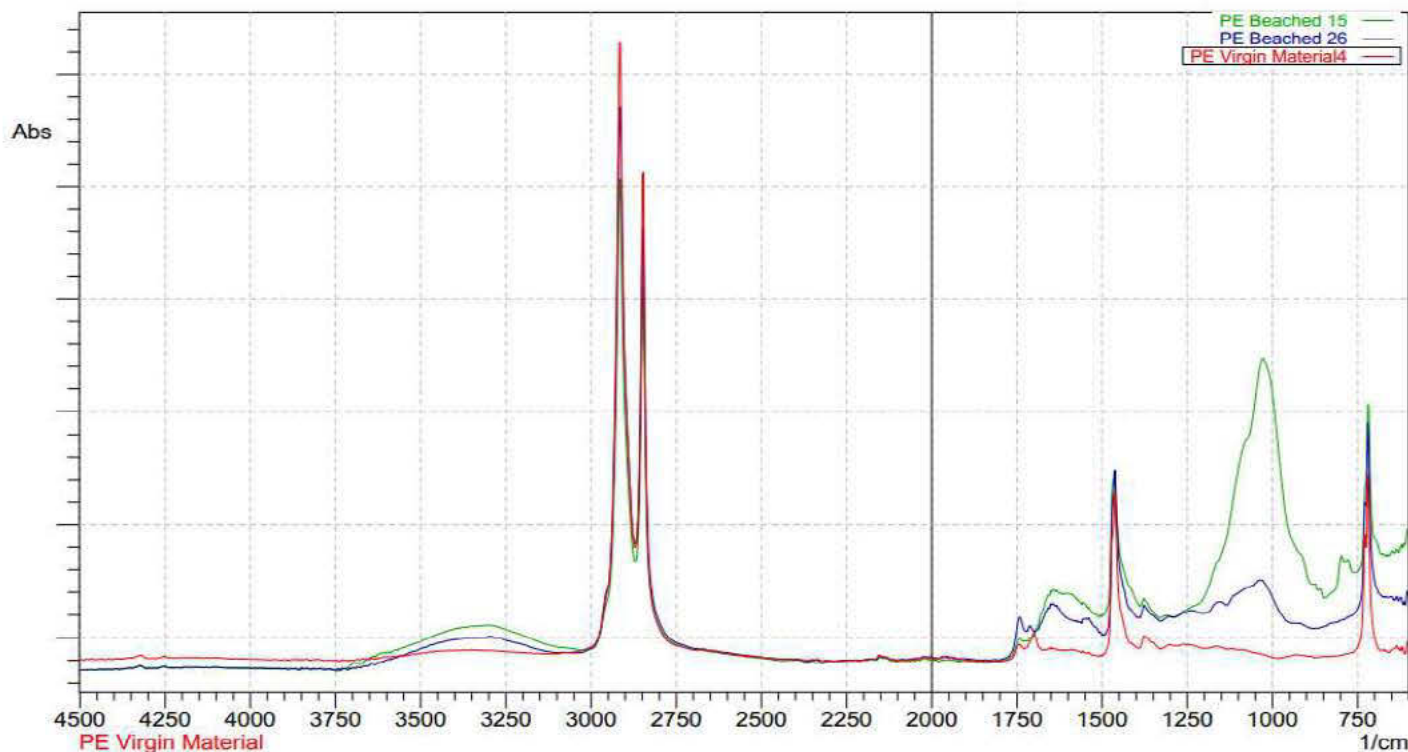




# Plastic in the environment, beached



Beached pellets are, especially on the surface, exposed to UV-radiation, heat and sand (grinding).



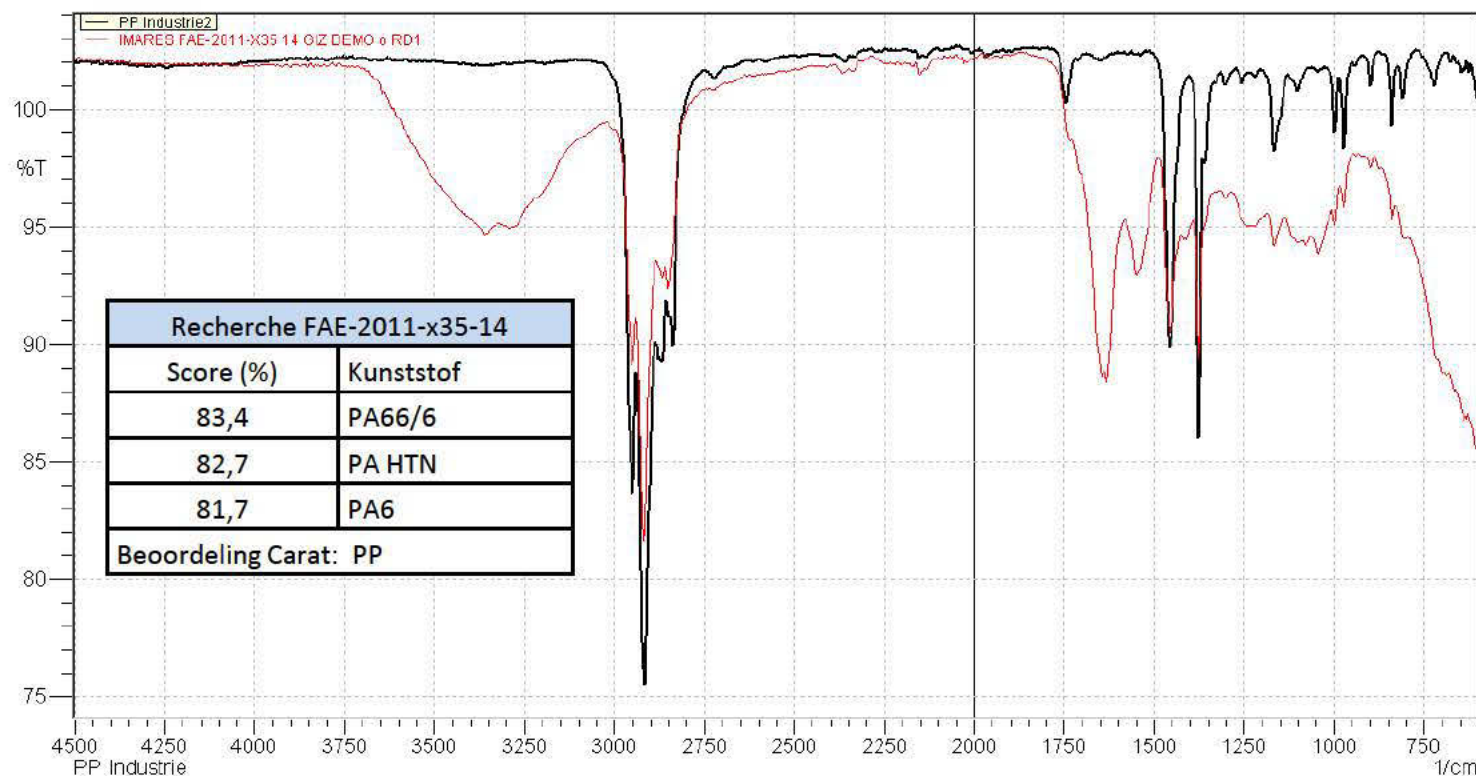
Changes in the surface are visible with FTIR-ATR.

The big green peak at 1090 cm<sup>-1</sup> is typical for sand (SiO<sub>2</sub>).

# Plastic in the environment, eaten



Some plastics, like PE, PP and EPS, float on seawater. Fulmars mistake floating plastic for food.



FTIR-ATR analyses of the unwashed samples gives a lot of additional peaks.

Standard library search results in PA (polyamide).

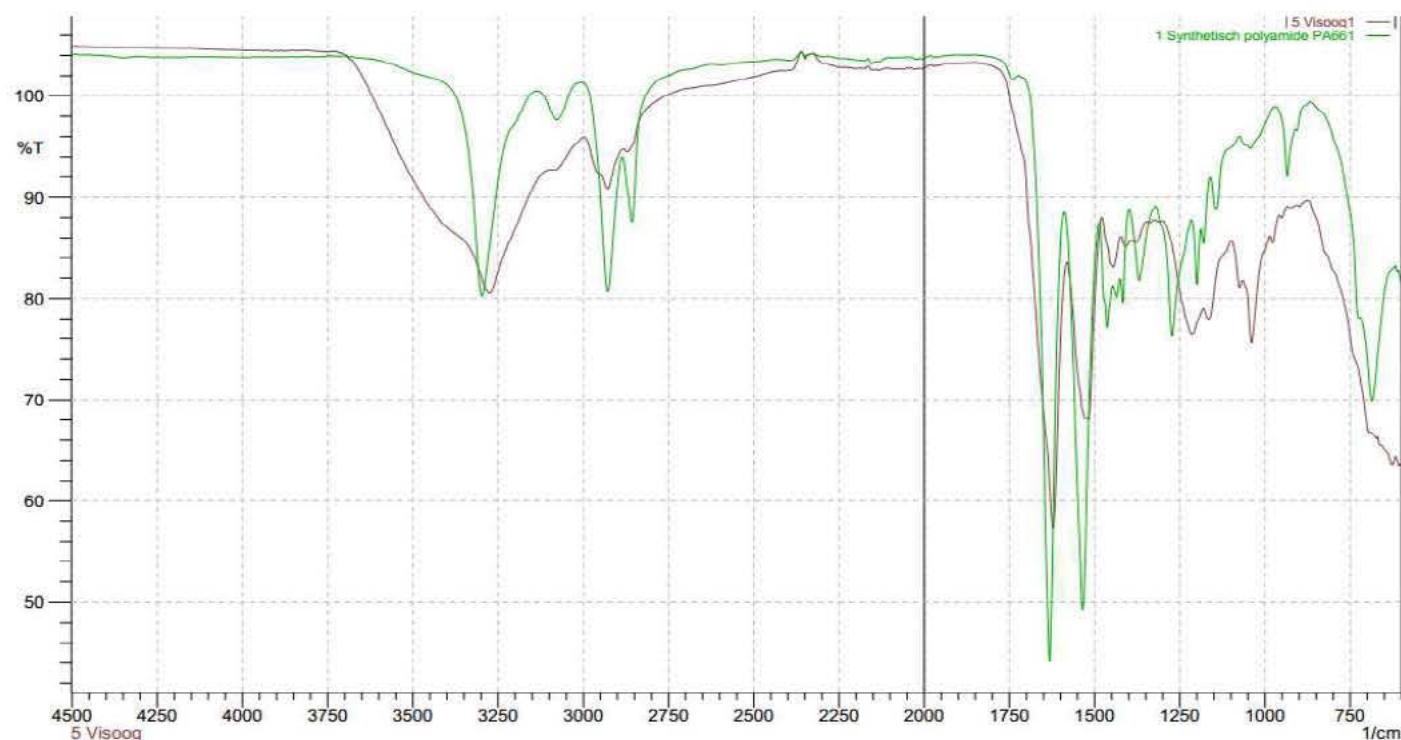
The PP pellet is on the surface contaminated with food-remains.



# Plastic in the environment, eaten

Another problem is that the libraries only contain spectra of synthetic polymers, it doesn't recognize polymers from nature, such as keratine.

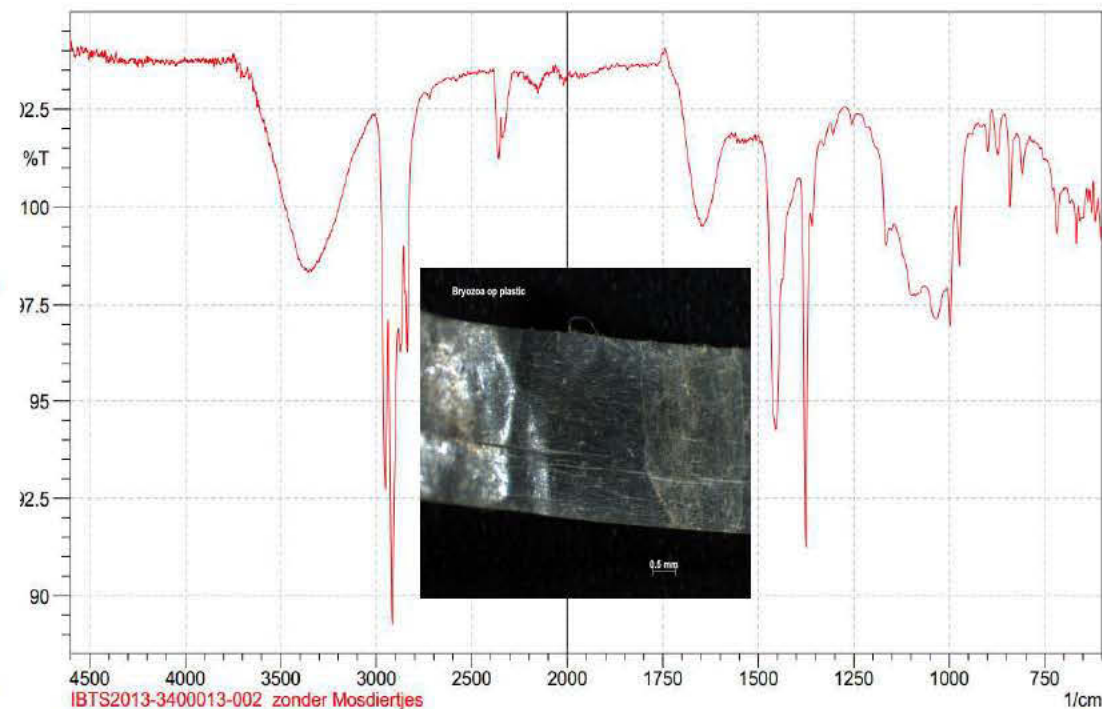
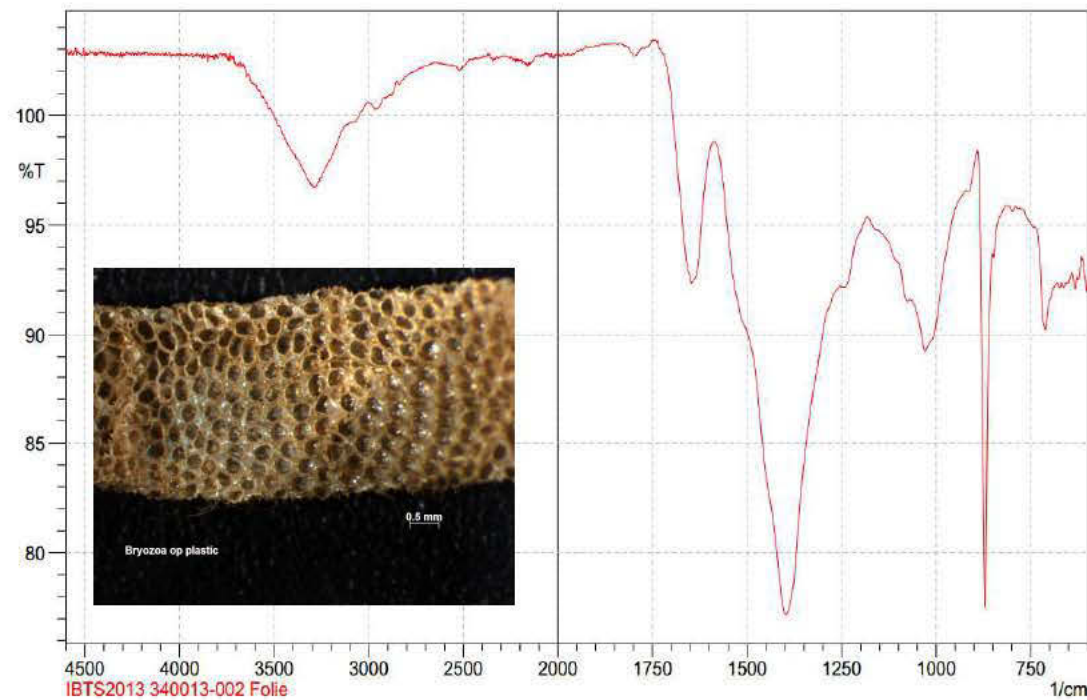
Keratine (black) vs  
synthetic nylon,  
PA66, (green)



A fish eye in the library search can easily interpreted as synthetic nylon (90% score).

# Plastic in the environment, biofouling

Biofouling, a biofilm forms on floatable plastics, the density becomes  $> 1,03 \text{ g/ml}$  and the material sinks in seawater.



The plastic ribbon is probably PP.

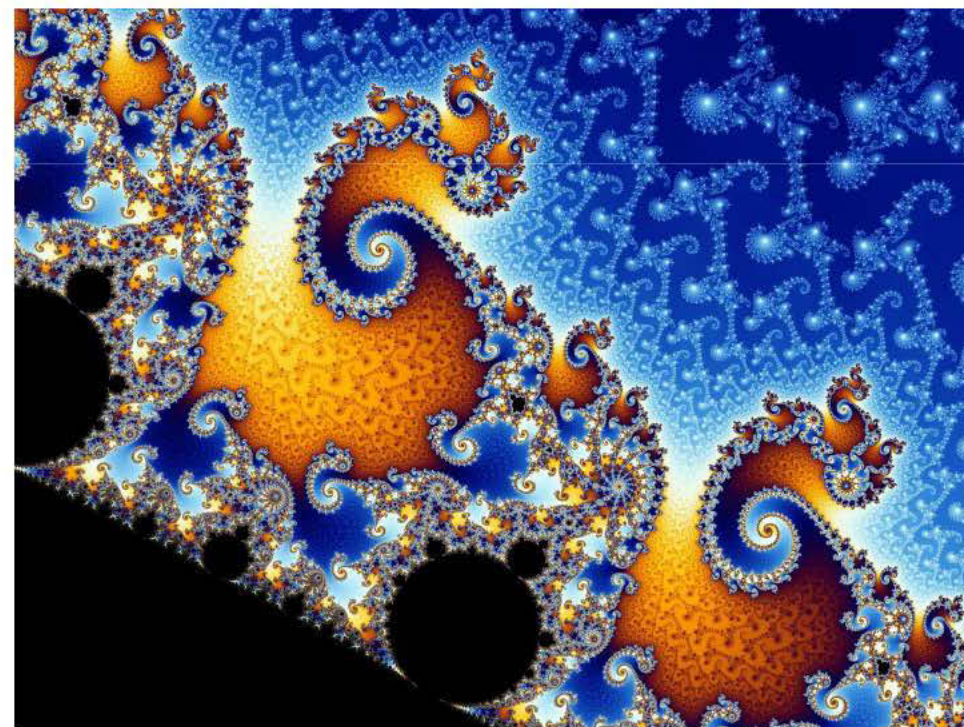


# Plastic in the environment

## Summary

Standard FTIR plastic libraries are excellent tools for describing virgin and pre-consumer raw materials.

For post-consumer and plastic in the environment these libraries doesn't fit ideal to use.



*Avoid logistic chaos*

Part of our research, in cooperation with Shimadzu and IMARES, is to develop a new approach to describe this kind of material in our new man-made society and environment.