

MATERIALS AND PRODUCTION CHEMICAL SOLUTIONS / COMPOSITE MATERIALS AND PRODUCT DEVELOPMENT



En standardiserad metod för glasfiberarmerade polymerer med avseende på mikroplast och framtida regler

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Abstract

Targeting a standardized method for glass fibre reinforced polymers with regards to microplastics and future regulations

Fibre reinforced polymers are strong and lightweight materials that are being used more and more commonly in many sectors. Due to the growing market size in areas such as automotive, building material, rotor blades of wind turbines the waste and waste management will become a coming problem in a near future. The increased use of plastics and composites have already induced environmental problems such as plastic and microplastics in the oceans, therefor there is a growing consciousness regarding microplastics and release sources of them into the environment. We have been targeting a standardized method for glass fibre reinforced polymers with regards to microplastics, environmental loads and future regulations. The results demonstrate that the tested reinforced polymers can be a source of microplastics. Results are presented with proposed attributes (25 analytical parameters) that can be used to classify samples/instances with regards to environmental loads. AI based machine learning techniques was used to classify the tested materials and create a training set on which two other plastics, the very common thermoplastic LDPE and the biodegradable thermoplastic PBAT, was tested with unambiguous indications. Finally, and quite interestingly, a new approach was tested for ultra-low detection of microplastics from these reinforced polymers. This Metal-enhanced fluorescence method utilized previously developed silver nanopillar SERS substrates, that can be bought commercially as of recently, demonstrating a general purpose of this method. Semi-optimized tests demonstrated remarkable femtogram detection limit of epoxy microplastics, which was also confirmed by surface mass-spectrometric TOF-SIMS with regards to plastic fragment identities.

Key words: Microplastics, glass fibre reinforced polymers, composites,

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1 Introduction

Plastics and composite materials are widely used today due to their unique properties gaining market size.1-3 Thermoplastics and thermosets are two different branches in this material group. Thermoplastics such as plastic bags are the most common plastic type and are the cause of today's big garbage dumps in the world's oceans.⁴⁻⁷ Thermosets are found to a lesser extent throughout the world, but are expected to have a growing waste mountain in a near future due to an increasing use in for example airplanes, cars and wind turbines.^{3,8,9} Fibre reinforced composites have excellent strength to weight properties, do not rust and have the ability to tailor properties to different applications.^{3,8,9} Therefore, the market for fibre reinforced composites is expected to grow in many different market segments despite some risk of negative environmental consequences and challenging recycling.9 It is therefore of utmost importance to ensure that the environmental impact is minimized or absent when using these materials.9 The project therefore aims to investigate whether external influences such as UV light, abrasion, leaching can produce micro / nanoplastics. As already mentioned, the thermoplastics is already identified as a source of microplastics in the oceans and therefore the project will focus in particular on thermosetting plastic composites in different environments such as saltwater, water and sediment. This to find out if it is better to equally bad to use thermoset composites over thermoplastics in marine applications. For this initial short study two water types, MilliQ and seawater, and no pre-treatment and 72 h of freezing at - 45 oC (potential to make the polymer brittle).10

Thermal aging behaviour of composites is of special interest because of their expanding use for structural applications where increased temperatures are common environmental conditions. Sometimes a sudden increase in temperature may be quickly followed by a sudden decrease in the temperature. There are significant chemical and structural changes in the fibre reinforced epoxy matrix composite, especially in the epoxy matrix networks, which take place during thermal aging. Delamination and micro-cracking are some of the most frequently observed damaging phenomena that may develop in polymer composites exposed to cryogenic temperatures (low-temperature conditions). It is important to understand the aging mechanism of polymer composites for their use in thermal aging environments or freeze/thaw environments. The mechanical behaviour of composites depends on the ability of the interface to transfer stress from the matrix to the reinforcement fiber.¹⁰

2 Material

For this study two different types of glass fibre reinforced polymers were selected, one with epoxy and one with polyester. The epoxy used was Huntsman Araldite LY 1564 / Aradur 22962. The polyester used was Polynt POLYLITE PO-4602. The material was selected as relevant composites to be used in applications with challenging environment. The plates were manufactured by vacuum infusion and cured according to supplier recommendation. Pictures of one of each sample can be seen in Figure 1.



Figure 1. Pictures of two of the studied reinforced plastic sample samples. Polyester on the right and epoxy on the left.

3 Methods and instruments

3.1 Standardized method SS-EN 12457-2

This Swedish Standard consists of the English version of the International standard EN 12457-2:2002, Characterization of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction).¹⁹

3.2 Image analysis

ImageJ image analysis software from National Institute of Health (NIH)20 was used with pre-defined functions for particle analysis and particle size distributions.

3.3 The Weka machine learning work bench

The use of artificial intelligence based machine learning algorithms was briefly tested with the openly accessed Weka machine learning work bench.^{21, 22} So far initial classification of the different sample types has been performed with promising results. This will be further assessed, and the results will be included in the up-coming article.

3.4 Instruments

Scanning electron microscopy (SEM); Zeiss Supra 40VP (Oxford Instruments)

Microscopy; Olympus BX63 with camera Olympus DP72 and lightsource X-cite Series 120PC

ICP – OES; Agilent 5110 ICP-OES

ICP – MS; Thermo Finnegan

XRF; Thermo Scientific Niton XL3t Gold

Ion Chromatography; Metrohm 930 Compact IC Flex

pH meter; Denver Instrument model 20 pH/conductivity meter

Conductivity; Knick Konduktometer 703

TDS; Heraeus Instruments oven D-6450 Hanau Type UT 6060, Scale Mettler Toledo AB135-S/FACT

TOF-SIMS; IONTOF GmbH

4 Results and discussion

4.1 X-ray fluorescence (XRF)

An initial XRF analysis of the composites shows that both contain approximately 1500 ppm Fe, 50 ppm Ni, 20 ppm Pb, 200 ppm Ba and high 7-10% Ca. One of four measurements on the epoxy plastic also showed 9.3 ppm of arsenic. The epoxy resin also shows 1000 ppm Cl. XRF is a semi-quantitative method so the values cannot be taken too accurately. The samples were further treated according to standardized method SS-EN 12457-2. To motivate the use of this method, normally applied on mixed waste from for example landfills. Specifically for these samples, the fact is that glass fibre reinforced polymers are extremely difficult to recycle and not really suitable for any energy conservation purpose (e.g. burn to get heat) due to the high content of glass. Therefore, GFRP materials commonly ends up in landfills. As the samples were large solid sheets the samples were cut to pieces and further crushed to fulfil the requirements of the method (95 % particle size below d = 5 mm). After which some samples were stored in a freezer for 72 h, and all samples were leached for 24 h in different types of water. Samples were decanted and filtered (on Cellulose acetate filters with pore size $0.45 \ \mu\text{m}$). On the filters mostly glass fibres were collected. The filtered water samples were further analysed with a number of techniques and methods, instruments and results are described below.

4.2 Chemical composition of the leached and filtered water samples according to SS-EN 12457-2

Chemical environmental loads of the samples were investigated in accordance with the standardized method (all results are displayed in table 1). Conductivity showed a decrease for the seawater samples on the order 20 and 30 μ S/cm for epoxy and polyester, respectively. For the MilliQ water samples the polyester showed an increase from 1.2 to 52.81 μ S/cm, and the epoxy increased to 32.82 μ s/cm. The pH measurements showed that the epoxy increased pH significantly in MilliQ water and somewhat in seawater, and more in the frozen samples. The polyester increased pH a little in MilliQ and decreased pH quite a bit in seawater (even more for the frozen sample). These results indicate that freezing may have had an impact on the samples.

ICP-OES and ICP-MS demonstrated some leaching of the tested elements. See table 1 for all detected elements. In brief, there were some aluminium in epoxy and none in polyester. More Cobalt (about 0.5 ppm) in all polyester water samples and close to zero in epoxy. More Hg in epoxy than polyester. Again, the epoxy showed small tendency to have arsenic within.

Ion chromatography was performed to test for anionic species such as nutrients and sulphate. Polyester released significant amounts of phosphate (10 times more than epoxy in MilliQ water). Both polymers leached some sulphate as indicated by the MilliQ water samples.

4.3 Solid material particles and size distributions in filtrate waters

Total solid material (TDS) was determined in the MilliQ water samples showing 39 and 97 mg/kg in the epoxy and polyester, respectively. 8 mg/kg leached water was also found in the blank MilliQ sample (which was also verified in e.g. SEM images). Hence, 31 and 89 mg/kg may be more accurate to consider as the contribution from the reinforced polymer samples, i.e. about 3 times more from polyester over epoxy. Microscope imaging demonstrated overall larger particles in the epoxy leached in MilliO water and more particles from polyester (Figure 2). By particle analysis in ImageJ the number of particles and size distributions was determined. Six microscopy images (3 for each material) were used to calculate particle numbers (Figure 3). The number of particles was determined to $12289 (\pm 3883, n = 3)$ and $49133 (\pm 6637, n = 3)$ per millilitre for epoxy and polyester, respectively. Particle size, defined as the Feret diameter, and distributions was and determined to 1.9 (\pm 0.4, n = 3) and 1.2 (\pm 0.1, n = 3) µm for epoxy and polyester, respectively. Surface coverage of particles was 1.62 % $(\pm 0.20, n = 3)$ and 2.73 % $(\pm 0.24, n = 3)$ for epoxy and polyester, respectively. This correlates well with previously mentioned TDS measurements as when transforming 2D - 3D percentages become 2.1 (range 1.7 - 2.5) and 4.5 (3.9 - 5.1), i.e. factor 2.87 (89/31) will fit in the intervals.



Figure 2. To the left: Microscopy images of filtrate of samples leached in MilliQ water (according to the standardized method SS-EN 12457-2). Scalebars are 10x1 μ m in size. Center: Thresholded images and overlay masks, particle analysis performed in ImageJ. Right: Particle Feret diameter distribution in pixels, one pixel equals 0.1 μ m, i.e. the mean values are roughly 1.6 and 1.1 μ m.

Figure 3. Feret diameter distribution in pixels for six microscopy images, epoxy on the upper row and polyester on the lower row.

4.4 Particle morphology

Scanning electron microscopy was used to see fine structures in the polymeric materials particle morphology (Figure 4– Figure 6). Overall, the polyester samples tended to demonstrate smaller particles.

Figure 4. Scanning electron microscopy images on the plastic samples leached in MilliQ water according to the standardized method SS-EN 12457-2.

Figure 5. Scanning electron microscopy images on the plastic samples leached in MilliQ water according to the standardized method SS-EN 12457-2.

Sea water filtrate

Figure 6. Scanning electron microscopy images on the plastic samples leached in Sea water according to the standardized method SS-EN 12457-2.

4.5 Label free Metal enhanced fluorescence detection of microplastics

Silver nanoparticle substrates were tested as an analytical tool to detect the microplastics in a fluorescence microscope. This Metal-enhanced fluorescence method utilized previously developed silver nanopillar SERS substrates,¹¹ that can be bought commercially as of recently,¹² demonstrating a general purpose of this method.

Benefits of the substrates:

1) The substrates are contaminant free after being prepared and sealed in clean-room facilities. $^{\rm 11,\,13}$

2) The substrates have a superhydrophobic and high adhesion surface keeping droplet imprint on the surface to minimum size and generating maximum evaporation concentration increase.^{14, 15}

3) The substrates possess plasmonic properties which likely are able to provide fluorescence enhancement on the order 10 - 1000 times.^{16, 17}

Considering the solid material found in the leached water samples 39 and 97 mg/kg in epoxy and polyester, respectively., as being 100 % from the composites (to have a not too low estimation). Then for the epoxy sample a 2 μ l droplet pipetted onto one of these goldnanopillar substrates will be a total amount of 78 ng epoxy loaded on the substrate. For the fluorescence image in Fig. 7, where there are 33313 fluorescent pixels the 78 ng can be considered to be distributed among them (i.e. about 2 pg per pixel). From noise levels (blank sample or dark spot in the same image, histograms Figure 7) and slope to the average fluorescence of the particles (right histogram Figure 7) a limit of detection (LOD) can be estimated (standard approximation 3*STDzero/slope).18 In this case

LOD was calculated to 47 and 42 fg, from the two different blanks. The limit of detection can here easily be improved by zooming in (Figure 8), however, for this image we have no "true" estimation of the total sample load in the image. As a simple approximation the LOD should improve inversely proportional to the magnification, i.e. here $5x - 20x \rightarrow LOD$ improves to the neighbourhood of 10 fg.

Figure 7. Microscopy image of the evaporated epoxy water sample droplet (upper left, 5x objective). Fluorescence image (excitation 365 nm and long pass RGB emission). Lower images and histograms displays the data used for Limit of detection (LOD)18 determination, which was estimated to 42 - 47 fg.

Figure 8. Fluorescence image of with a 20x objective of the evaporated epoxy water sample. Limit of detection $(LOD)^{18}$ was estimated to 10 - 12 fg, which correlates well with the estimation on the 5x objective fluorescence image (Fig. 7).

Sample	1	2	3	4	5	6	11	12
Plastic	Ероху	Ероху	Ероху	Polyester	Polyester	Polyester	Blank	Blank
Watertype	MilliQ	Sea	Sea	MilliQ	Sea	Sea	MilliQ	Sea
Treatment	No	No	Freeze	No	No	Freeze	No	No
Parameter								
Cond.(µS/cm)	32.82	10850	10850	52.81	10840	10840	1.2	10870
рН	8.25	7.82	8.06	5.80	6.79	6.63	5.55	7.48
Hg (ppb)	0.067	0.041	0.049	0.025	0.020	0.018	0.005	0.004
As (ppm)	0	0.007	0.012	0	0	0	0	0.005
Co (ppm)	0.001	0.004	0.001	0.420	0.454	0.468	0	0
Cu (ppm)	0	0.003	0.006	0.016	0.022	0.02	0	0
Mo (ppm)	0.002	0.005	0.002	0	0.003	0.001	0	0
Ni (ppm)	0	0.003	0.003	0.007	0.007	0.007	0	0.003
Zn (ppm)	0.002	0.043	0.038	0.089	0.084	0.066	0	0
Al (ppm)	3.57	0.630	0.900	0	0	0	0	0
B (ppm)	0.32	0.88	0.86	0.69	1.05	0.96	0	0
Ca (ppm)	4.56	69.05	70.57	7.72	71.85	71.18	0	64.01
Mg (ppm)	0.37	187	189	0.85	193	185	0	188
Na (ppm)	0.33	33.35	33.91	0.3	30.42	31.79	0	31.52
Si (ppm)	0.71	3.64	3.71	1.59	4.29	4.22	0	3.84
PO4 (mg/L)	0.18	0.00	0.00	1.79	1.44	1.23	0.02	0.00
NO3 (mg/L)	0.04	1.45	0.99	0.08	1.53	1.57	0	1.41
SO4 (mg/L)	0.58	358	354	0.39	374	370	0.05	370
Br (mg/L)	0	9.71	9.55	0	9.91	9.80	0.04	9.52
Cl (mg/L)	0.25	355	356	0.06	357	353	0.07	352
F (mg/L)	0.15	0.71	0.63	0.17	0.19	0.18	0.00	0.54
TDS (mg/kg)	39	39	39	97	97	97	8	8
Part. Feret d (µm)	1.9	1.9	1.9	1.2	1.2	1.2	0	0
Part. Area%	1.62	1.62	1.62	2.73	2.73	2.73	0	0
N particles/ml	12289	12289	12289	49133	49133	49133	0	0

Table 1. Measurement data from filtered leached sample waters (according to a standardized method for waste materials: SS-EN 12457-2).*

* Pb, Cd, Sb, Cr, Fe, Ba, Be, Bi, Se, Sn, Tl, V, Ba, Ag, Li < Below limit of detection for all samples.

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5 Conclusions

The risk of emitting micro- and nano plastics from glass fibre reinforced epoxy and polyester has been investigated. The investigation methods were grounded in standardized method SS-EN 12457-2 for waste particulate materials and its filtrate measurement methods. Additionally, different microscopy techniques were used to characterize the materials. The results demonstrate that the tested reinforced polymers can be a source of microplastics. The number of particles was determined to 12289 (± 3883, n = 3 and 49133 (±6637, n = 3) per millilitre for epoxy and polyester, respectively. Particle size, defined as the Feret diameter, and distributions was and determined to 1.9 (\pm 0.4, n = 3) and 1.2 (\pm 0.1, n = 3) µm for epoxy and polyester, respectively. Surface coverage of particles was 1.62 % (± 0.20 , n = 3) and 2.73 % (\pm 0.24, n = 3) for epoxy and polyester, respectively. Which also confirms the solid material found in the leached water samples 39 and 97 mg/kg in epoxy and polyester, respectively. In conclusion, these particle results indicate that the polyester based material tends to generate not only more material overall, but also larger number of particles that are on average 40 % smaller. Other not insignificant environmental loads may be phosphate from the polyester and small amounts of As/Hg from the epoxy.

Future research of interest for us would be to further assess the Weka machine learning work bench to develop a complete standardized concept, possibly including more parameters of interest, for accurate classification of reinforced polymers for future regulations.

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