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Deliverable report

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Project Website:	www.creatorproject.eu

CREATOR CONSORTIUM

PARTICIPANT NUMBER	ABBREVIATION	ORGANISATION
1	ICT	Fraunhofer Gesellschaft für angewandte Forschung – Institut für Chemische Technologie
2	VLB	Volbas S.A.
3	MOS	Machinefabriek Otto Schouten BV
4	CLR	Coolrec BV
5	REL	TREEE – Treatment and Recycling of Electrical & Electronic Equipment
6	GKR	Fundacion Gaiker
7	TCK	Transfercenter fur Kunststofftechnik GmbH
8	RMA	Erema Engineering Recycling Maschinen und Anlagen Ges.m.b.H
9	CTB	Centre Scientifique & Technique De L'industrie Textile Belge
10	MAI	Maier S. Coop.
11	DAW	DAW SE
12	CYC	Cyclefibre S.L.
13	CID	Fundacion Cidaut
14	KLU	Kuhne Logistics University GmbH
15	OVM	Openbare Vlaamse Afvalstoffenmaatschappij
16	RWE	RWEnergia Robert Wudarczyk
17	ITB	ITRB Group LTD

DOCUMENT HISTORY AND CONTRIBUTION OF THE PARTNERS

Table 1: Version management

VERSION NR	REVISER	CONTENT
1	ICT	Report description
2	CTB	Revision 1
3	ICT	Revision2
4	ICT	Submission

Table 2: Partners' contribution to the deliverable

PARTNER	SHORT NAME	ROLE IN THE WP	CONTRIBUTION TO THE DELIVERABLE
Fraunhofer ICT	ICT	Lead WP3	Screening trials with co-sovlents and CO2, continuous supercritical CO2 extrusion trials.
Centexbel	CTB	Lead Task 3.2	Supporting activities in Task 3.1 and Task 3.5

ABBREVIATIONS

ABS	Acrylonitrile butadiene styrene
C&DW	Construction and demolition waste
DAD	Diode array detecto
EEE	Electrical and electronic equipment
EPS	Expanded polystyrene
HBCD	Hexabromocyclododecane
HPLC	High pressure liquid chromatography
MS	Mass spectroscopy
NADES	Natural deep eutectic solvents
PA	Polyamide
PC	Polycarbonate
POP	Persistant organic pollutants
PS	Polystyrene
PP	Polypropylene
PU	Polyurethane
sc-CO_2	Supercritical CO_2
TGA	Thermogravimetric analysis
WEEE	Waste electrical and electronic equipment
XRF	X-ray fluorescence spectroscopy

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1 INTRODUCTION

The EU funded project CREAToR focuses on process development and demonstration (to TRL 5) to remove hazardous, already banned bromine containing flame-retardants from waste streams using continuous purification technologies: supercritical CO_2 and cost-effective solvent-based processes using natural deep eutectic solvents (NADES) in twin-screw extruders.

CREAToR will cover the whole value chain, starting from collecting thermoplastic waste streams from construction and demolition waste (C&DW) and construction and from waste electrical and electronic equipment (WEEE). The project will implement ways to collect secondary raw materials, identify the presence of hazardous flame retardants, remove these contaminants from the materials and finally reuse the materials.

As case studies they will be reused as valuable secondary raw materials for new B&C insulation panels, closing the circle of economy, for automotive interior application, and for producing 3 D printed parts for aerospace applications. For further increasing the economic feasibility of the approach an optimised logistic concept and a harmonized material quality classification scheme will be developed and applied.

In this deliverable D3.1 a continuous extrusion technology, the so-called extractive extrusion process, is presented to demonstrate the potential to remove HBCD fire retardants from a polymer matrix by the use of supercritical CO_2 (sc-CO_2) with and without co-solvents.

The extractive extrusion process technology is an advanced extrusion process. Its unique key characteristic is the melt purification via sc-CO_2 which is brought in and out of the extruder in a supercritical state. The non-legacy substance, e.g. HBCD, is dissolved in the sc-CO_2 and redirected out of the extruder.

The focus of the study is to extract HBCD from a polystyrene (PS) foam material, which was used as isolation material in the building sector in the previous decades. Apart from building isolation materials, HBCD was also detected in ABS coming from WEEE and fridges. However initial screening trials showed only low amounts of HBCD in ABS. Consequently, the ABS fraction has not been used as second grade to optimize the extractive extrusion process for the removal of HBCD.

Furthermore, PC, PA and PU are also not included in this study, as these materials are only available in limited amounts and therefore only of little interest.

The initial experiments started in a batch scale in order to study the extraction efficiencies of diverse solvents at different conditions (temperature, pressure). Afterwards the parameters were transfered to continuous processing. The report contains the results of two experimental campaigns carried out at Fraunhofer ICT's lab using the extractive extrusion process.

2 MATERIALS AND METHODOLOGIES

A literature study of potential solvents (and processing parameters) for batch and extrusion processing (extraction of HBCD, bromides etc.) was carried out. Potential solvents which have been identified are: acetone, acetonitrile, 1-propanol, 2-propanol, 1,4-dioxane, toluene.

The target of this study is to identify the extraction efficiency of the solvents used. For this, ca. 1 g of HBCD (1,2,5,6,9,10-hexabromocyclododecane) was placed in a 40 ml bottle. Then 10 ml of the solvent was added and stirred for one hour. Subsequently the filtration of the suspension evaporation at 40 °C in a vacuum drying cabinet was carried out. The results showed that the best solubility was achieved with acetone (8,6 g/100 mg), 1,4-Dioxane (8,4 g/100 mg), toluene (9,9 g/100 mg), 1,4-Dioxane 2 (9,5 g/100 mg).

In a second step a thermogravimetric analysis (TGA) was carried out to investigate the thermal decomposition temperature of pure HBCD. The TGA was carried out in an inert gas atmosphere. The result showed that HBCD decomposes in one stage in the temperature range of 220 - 260 °C. The total mass loss is

approximately 95 % which results in a residual mass of 5 % after reaching 300 °C. The graph indicating the decomposition of HBCD depending on tempeature under inert gas is shown in

Figure 1.

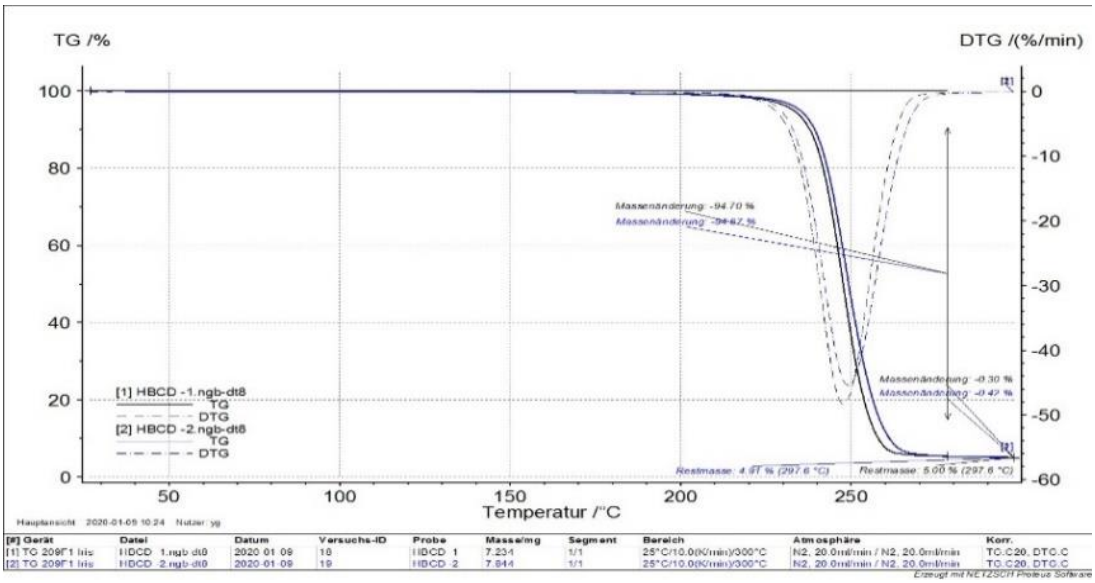


Figure 1: TGA results of pure HBCD

2.1 C&DW PS FOAM: MATERIAL PREPARATION FOR HBCD EXTRACTION

Old insulation boards containing expanded polystyrene (EPS) and HBCD were supplied by the project partner DAW for the extractive extrusion investigations. The first step was to prepare the foamed boards for futher processing. In a compaction step the boards were squeezed using a large-scale press equipment and ground to obtain easy to dose granulate material. Figure 2 shows the foamed boards before (left) and after compaction (right).

Figure 2: Foam boards before (left) and after compaction (right)

In the next step exemplary pieces of the shreddered fractions were selected to identify the HBCD content via HPLC MS analysis. In the study toluene and methanol were used as solvents. The results indicated a content of 1.18 % HBCD in the PS material.

2.2 SOLVENT EXTRACTION OF PS SAMPLES (BATCH)

The results of the solubility test showed that acetone is highly efficient to dissolve HBCD. As acetone is also - among the considered solvents - the least critical solvent concerning human and environmental health, the further extraction tests focussed on acetone.

To further investigate the extraction efficiency of acetone for HBDC, shreddered fractions of the foamed boards described above are used. For this, the HBCD boards have been brought into an autoclave with acetone and treated under different conditions concerning temperature, pressure and extraction time. An overview of the HBCD board extraction trials at different conditions (type of gas and gas pressure) is given in Table 3. The ratio of HBCD boards to solvents was 1:3 (g/ml). The decants, the solvent with the extracted substance, were isolated and analysed.

Table 3: HBCD boards extraction trials at different temperature and CO2 loadings.

SAMPLE NO.	TEMPERATURE IN	GAS	PRESSURE AT BEGINNING IN BAR
CreatorSE_1	200	-	-
CreatorSE_2	100	N_2	8
CreatorSE_3	100	CO_2	40
CreatorSE_4	150	CO_2	40
CreatorSE_5	200	CO_2	40
CreatorSE_6	200	CO_2	40
CreatorSE_7	150	-	-
CreatorSE_8	150	CO_2	50
CreatorSE_9	20	-	-
CreatorSE_10	200	-	-
CreatorSE_11	100	-	-
CreatorSE_12	150	CO_2	40
CreatorSE_13	100	CO_2	40
CreatorSE_14	125	CO_2	40
CreatorSE_15	100	CO_2	50

CreatorSE_16	20	-	-

2.3 SUPERCRITICAL CO_2 EXTRACTION

After the solvent extraction in batch, the next step was to transfer the experience gained to the continuous extrusion process. For this reason, the extractive extrusion process was set up to continuously remove HBCD from the PS melt. The process scheme is shown in

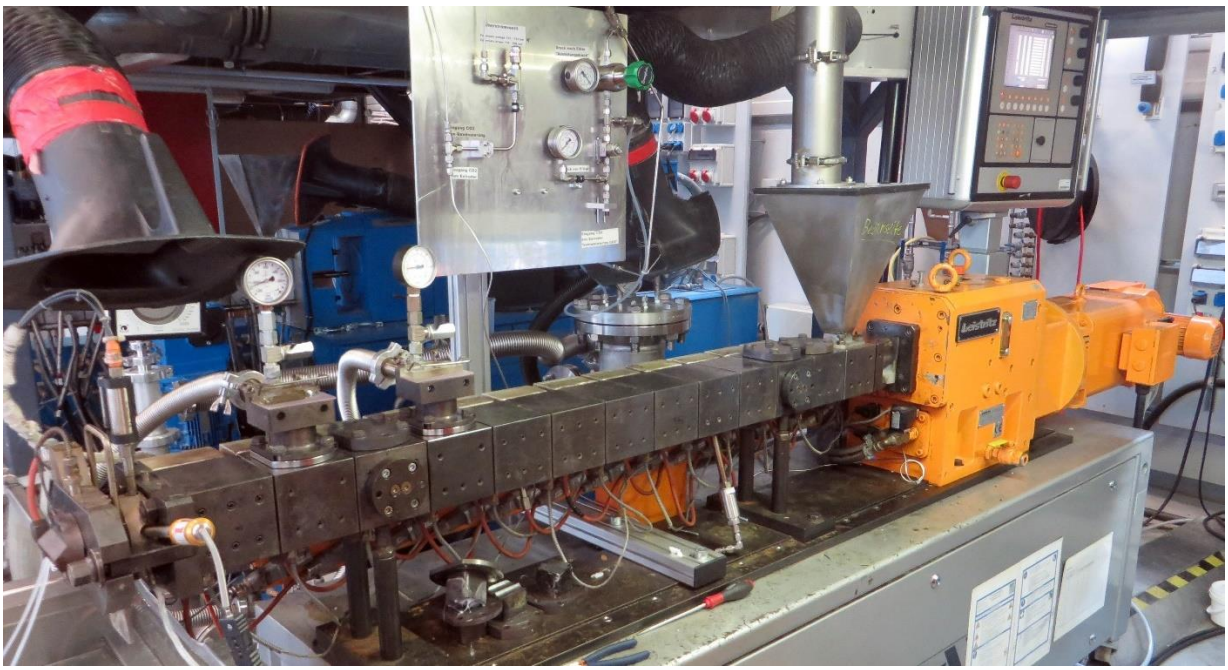
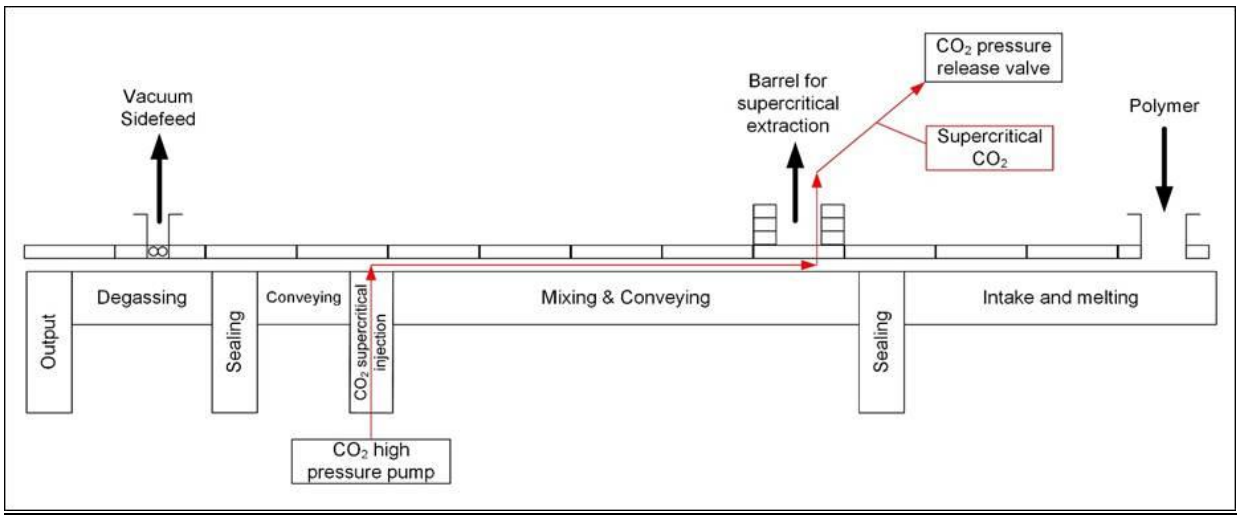


Figure 3.



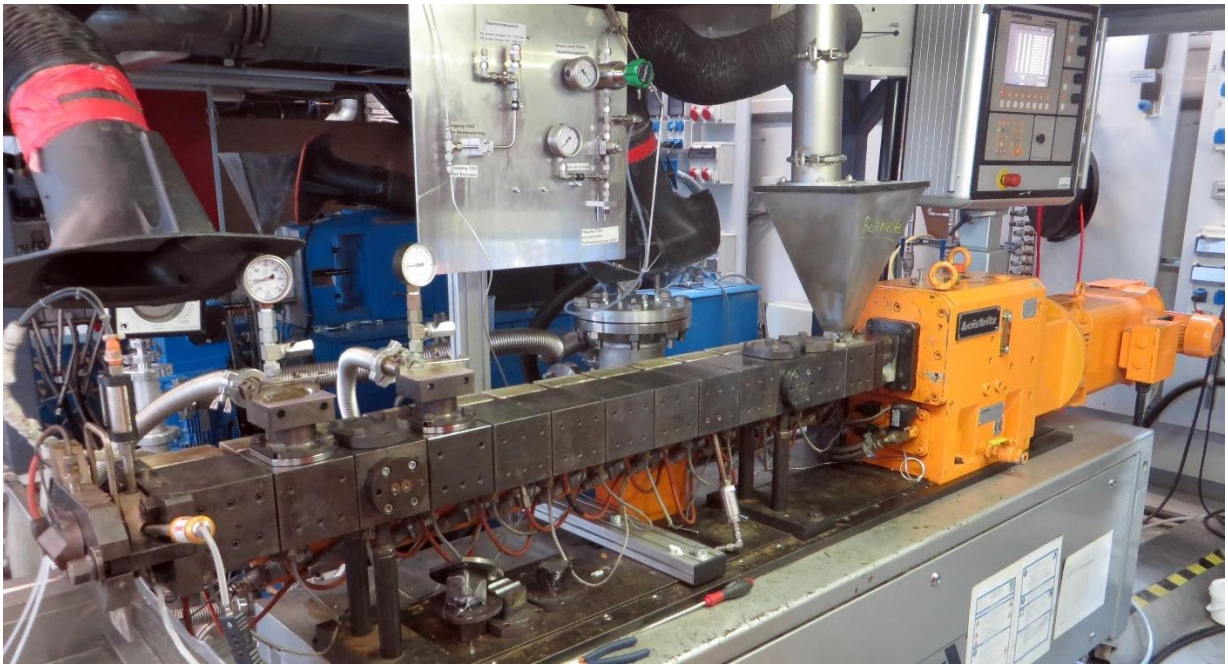


Figure 3: Extractive extrusion process to continuously remove HBCD from PS melts: schematic view (above) and the the real process (below)

On the right side of the process scheme, the contaminated PS polymer is fed into the extruder via the hopper. Afterwards the molten polymer in the melting zone is further transported into the "mixing and conveying" zone. The "mixing and conveying zone" is characterized by two melt seals which allow a pressure build up. Within this zone sc-CO_2 is fed via a gas dosing system. CO_2 reaches the supercritical state of aggregation at a pressure above 73.75 bar and a temperature above 30.98 °C.

During the mixing of polymer melt and sc-CO_2 the HBCD can dissolve and be extracted into the sc-CO_2. The addition of a co-solvent such as acetone should further enhance the dissolution potential and therefore the extraction efficiency. After extraction, the sc-CO_2, the co-solvent and the contaminent HBCD are fed into a phase-separator, in which the extracted HBCD is separated from the sc-CO_2 and the solvent and retained for disposal. At the extruder die the purified polymer melt leaves the extruder.

For the extractive extrusion trials an intensive safety and risk assessment including risk assessment for the staff and equipment was carried out. In this context the max. acetone content to operate the line below the lower explosion limit was calculated. Further, the requirements for the phase separator to separate the HBCD from the output stream were defined and accordingly a phase separator was purchased.

2.4 HBCD EXTRACTION METHOD

For the extraction tests 1 g of materials was mixed with 20 ml toluol/MeOH (60/40 v/v) and treated in an ultrasonic bath for two hours at 80 °C for extraction. Afterwards, the solution was filtered over a blue band filter into a 100 ml volumetric flask and filled up with the solvent mixture. The samples were filtered again before the HPLC-MS measurement over a 0.2 µm syringe filter.

2.5 HBCD ANALYSIS

The following tables show the HBCD analysis via HPLC-MS. Table 4 shows the equipment used and Table 5 shows the eluent gradient.

Table 4: Parameter of HPLC MS IonTrap XCT+ series 6330 Agilient Technologies.

EQUIPMENT	TYPE NAME
Analyser	HPLC1200SL
Ion source	MMAPESI negative mode
Eluent A	MeOH, ms grade/water (75/25 v/v)
Eluent B	Acetonitrile, ms grade
Flow rate	0.3 ml/min
Column	ZORBAX SB C-18, 2.1x150mm, 5 µm
Oven temperature	20 °C

Table 5: Eluent gradient in HPLC analysis.

TIME [MIN]	B [%]
0.0	20
1.0	20
1.1	55
11.0	55
11.1	20
20.0	20

The methodology first used was to determine HBCD via an evaporated light scattering (ELS) detector. A mix of different HBCD standards was used. The measured HBCD-content was not reproducible. The method was therefore further developed and individual standards α-, β-, γ-HBCD and a mixture of them were ordered for the calibration of the HPLC system. The most stable HBCD isotop with a m/z ratio of 640.5 was used for the calibration. The mass number represents the most stable crystallisation phase of the HBCD fragments. Figure 4 shows the calibration curves of the individual standards.

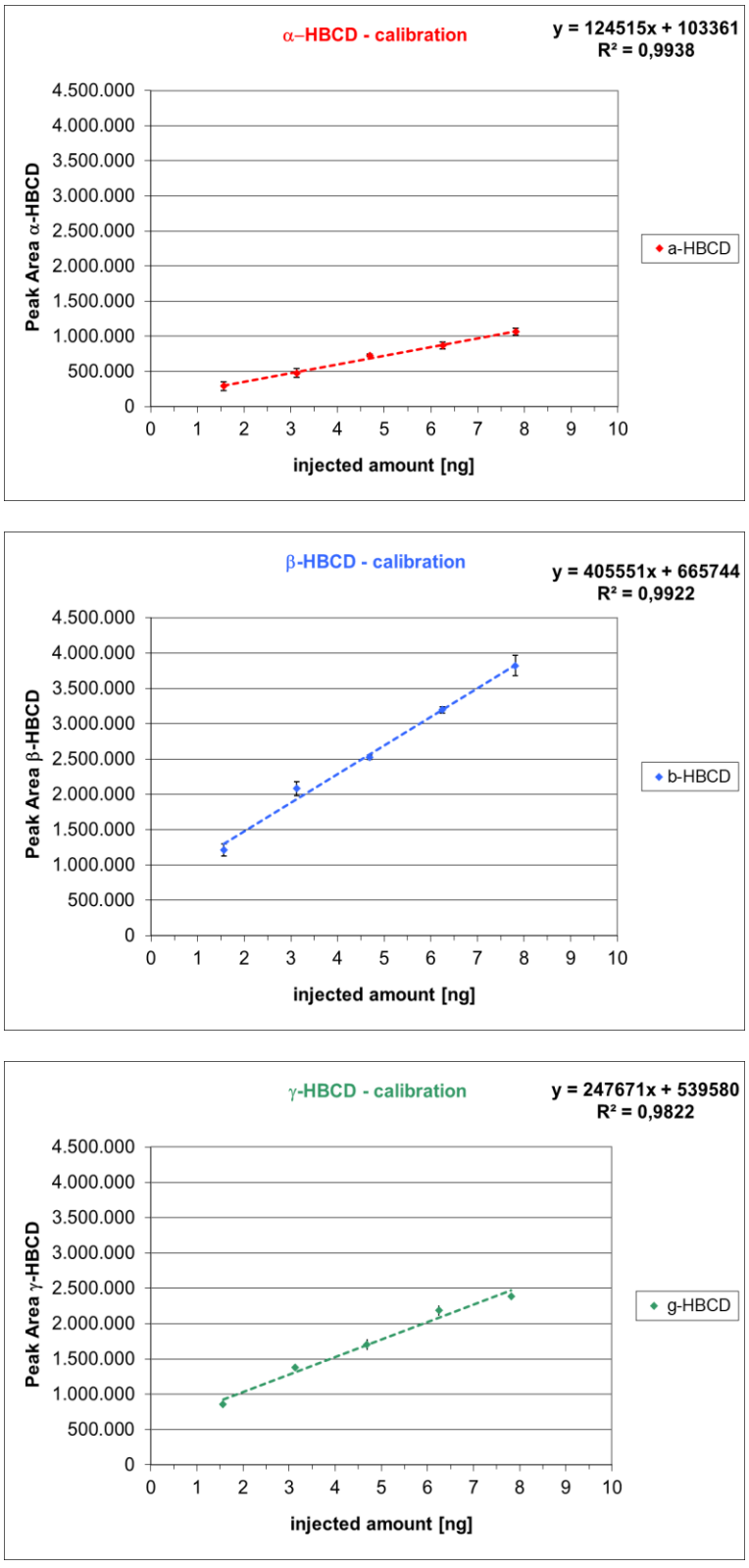


Figure 4: Result of external calibration procedure with EIC 640.5 +/- 0.5, integrated peaks (subtracted peak start and end, exclusion mass filter: 50 to 630 and 650 to 800 amu).

3 RESULTS

3.1 RESULTS ON SOLVENTS' EXTRACTION EFFICIENCY IN BATCH INVESTIGATION

The results showed the extraction of a white powder. Additionally, the decants showed different colors and a noticeable variation in the amount of powder. In Figure 5, the different colored decants and the residual with powder are shown.

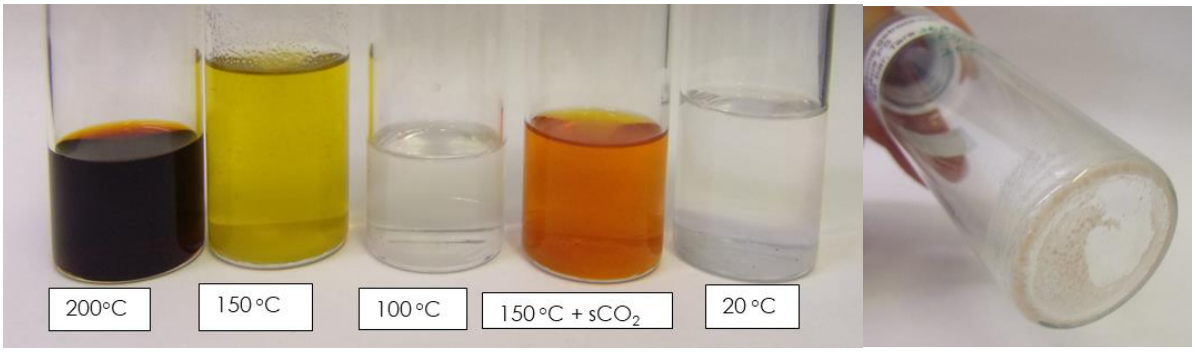


Figure 5: Decants of the extraction tests showing different colors, (left) for CreatorSE_6, CreatorSE_12; CreatorSE_3, CreatorSE_8, CreatorSE_16 (from left to right) and extracted white powder of CreatorSE_16 (right)

In the next step, GPC analyses to investigate the effect of acetone and the treatment conditions on the molecular weight of the PS, and GC-MS analyses to investigate the composition of the flakes were performed. Table 6 shows the results of the GPC analysis.

Table 6: HPLC results of dried HBCD boards after extraction.

SAMPLE NO.	MW IN G/MOL	POLYDISPERSITY
REFERENCE MATERIAL	173.200	2,46
CreatorSE_1	80.215	2,54
CreatorSE_2	161.940	2,35
CreatorSE_3	188.880	2,45
CreatorSE_4	181.400	2,36
CreatorSE_5	69.491	1,90
CreatorSE_6	68.298	2,14
CreatorSE_7	167.880	2,30
CreatorSE_8	153.760	2,28
CreatorSE_9	222.580	2,60
CreatorSE_10	137.080	2,64
CreatorSE_11	209.860	2,44
CreatorSE_12	195.790	2,39
CreatorSE_13	194.830	2,44
CreatorSE_14	198.040	2,38
CreatorSE_15	203.140	2,45
CreatorSE_16	206.150	2,31

As can be seen in Table 67, the molecular weight of the PS samples decreases with higher reaction temperatures, most significantly at 200 °C. At the end of the extraction at 150 °C, there is a slight decrease, and for the trials at 100 °C an increase in the molecular weight is visible. Additionally, a GPC measurement with a DAD detector was made to determine the HBCD content in PS; however, the molecular weight of the HBCD was too low and thus no visible peak was detectable.

The HBCD analysis was implemented at the HPLC system and the method of partner Centexbel was adapted to obtain more comparable data for further elaboration. As shown in Table 7 the results for the liquid phase analysis spread a lot, also due to the fact that the decant was not hard to handle due to the high viscosity of PS board residue after extraction trials. The solvents and probably also HBCD stuck into this matrix. The solid residue was therefore also analysed by the HPLC method. The results are summarized in Table 7.

Table 7: Analysis of decant solution after extraction trials and solid HBCD board.

SAMPLE NO.	T IN °C	HBCD-CONTENT IN % IN LIQUID PHASE	HBCD-CONTENT IN % IN SOLID PHASE
CreatorSE_1	200	0	0
CreatorSE_2	100	19,98	0,138±0,009
CreatorSE_3	100		0,1±0,011
CreatorSE_4	150	12,04	0,281±0,003
CreatorSE_5	200	0	0
CreatorSE_6	200	0	0
CreatorSE_7	150	16,03	0,085±0,024
CreatorSE_8	150	8,31	0,1055±0,0145
CreatorSE_9	20	33,73	0,484±0,102
CreatorSE_10	200	0	0
CreatorSE_11	100	14,7	0,183±0,012
CreatorSE_12	150	18,97	0,1225±0,0215
CreatorSE_13	100	40,33	0,2175±0,0215
CreatorSE_14	125	27,49	0,1315±0,0255
CreatorSE_15	100	35,3	0,276±0,025
CreatorSE_16	20	12,51	0,000

As can be seen in Figure 6, the HBCD content in the solid material after extraction decreases with increasing temperature. One exception is the trial at 20 °C with no HBCD content. This sample was washed five times with a solvent at room temperature in order to check the extraction of HBCD just by stirring and solvent refreshing. After each washing step the solvent was removed and refreshed. Even at 200 °C, no HBCD was visible (Table 7).

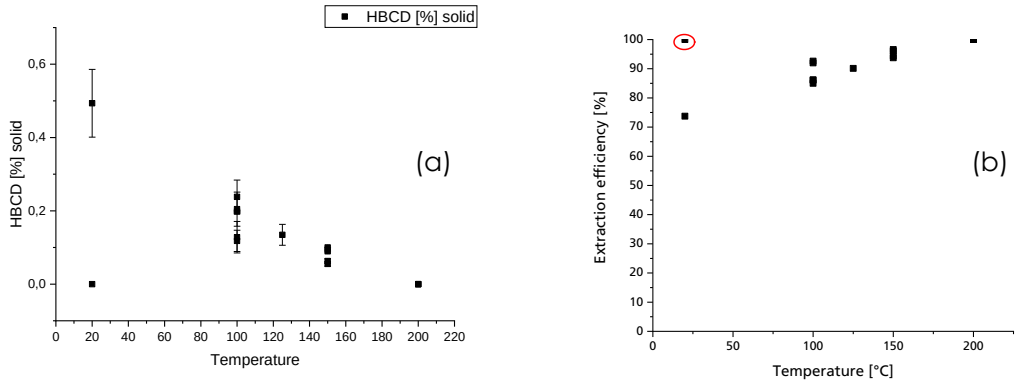


Figure 6: HBCD content in solid PS board samples after extraction trials (a) and extraction efficiency of HBCD removal [%] (b).

Figure 6 shows the the efficiency of HBCD extraction. It can be observed that at 100 °C there is already an extraction efficiency of over 80 %, and at 200 °C 100 % of HBCD is removed. Due to the difficult handling of the reaction mixture, the data was cross checked via an XRF measurement related to the bromine content, to ensure that a removal of other bromine organic components can be excluded. The measurements were only performed for the extraction trails performed at 200 °C. The results are shown in Table 8.

Table 8: XRF measurements of solid HBCD boards after extraction at 200 °C

SAMPLE NO.	UNITS	BR	BR ERROR ±	% HBCD
CreatorSE_1dried	ppm	797	32	
CreatorSE_1 dried	ppm	736	31	
CreatorSE_5 dried	ppm	1547	50	
CreatorSE_5 dried	ppm	1520	49	
CreatorSE_6 dried	ppm	1682	39	
CreatorSE_6 dried	ppm	1651	39	
CreatorSE_10 dried	ppm	2188	55	
CreatorSE_10 dried	ppm	2168	53	
CreatorSE_16 dried	ppm	926	32	
CreatorSE_16 dried	ppm	906	32	
CreatorSE_9 dried	ppm	4704	134	
CreatorSE_9 dried	ppm	4666	133	
CreatorSE_12 dried	ppm	4476	97	
CreatorSE_12 dried	ppm	4530	95	
CreatorSE_13 dried	ppm	3868	87	
CreatorSE_13 dried	ppm	3793	85	
Reference material	ppm	9214	179	1,222

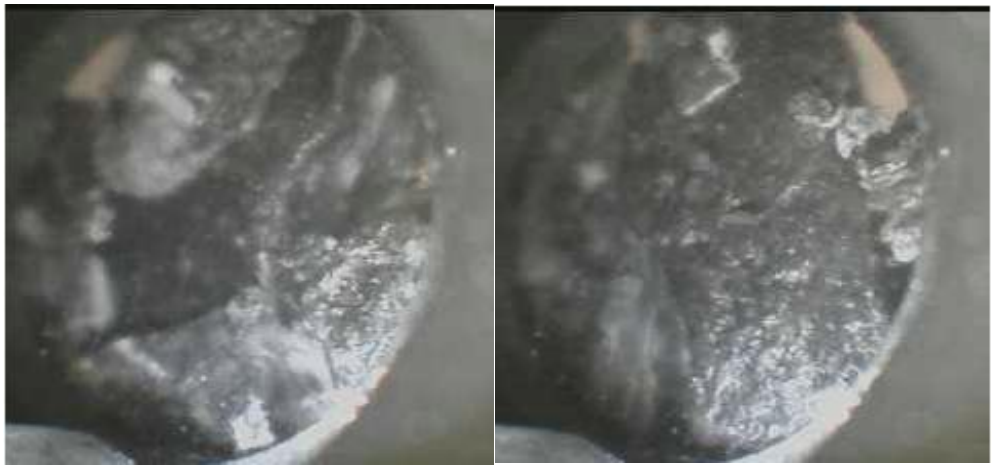


Figure 7: PS board images of XRF bromine content analysis.

It can be observed that bromine is still present in the sample, either in the form of inorganic bromine salt or as an organic component. In the HPLC analysis, secondary peaks appeared next to the main peak of HBCD. A GC-MS analysis was therefore carried out to determine whether they showed the presence of HBCD's decomposition components, produced during the extraction trials.

3.2 Results on sc-CO_2 extraction efficiency in continuous extraction process

3.2.1 Extractive extrusion trials – first campaign

The first extractive extrusion trials have been carried out using compacted and shreddered HBCD-containing PS from DAW insulation boards (as described above). The extruder set-up was selected to ensure soft processing conditions. A moderate screw speed of 150 rpm and a moderate temperature level of 170 °C were used. The polymer throughput was set to 5 kg/h for all samples. The first sample C-018 is the reference sample, which does not undergo any extraction with sc-CO_2 or a co-solvent but which passes through the processes using the same parameters as used for the other samples. The second sample, C-019, is only treated with sc-CO_2 for extraction and the third sample, C-021, is additionally processed with acetone. Table 9 shows the experimental set-up of the first campaign.

Table 9: Experimental set-up – first campaign

Trial		Extruder		Extraction			
#	Materials	T (°C) (extrusion zone)	speed rpm	throughput PS	throughput CO2	Throughput Acetone	Injection pressure gas/aceton
				kg/h	kg/h	kg/h	bar
Creator_018	EPS Compacted	170	150	5	0	0	0
Creator_019	EPS Compacted	170	150	5	3	0	99
Creator_021	EPS Compacted	170	150	5	3	0,15	90/80

The resulting samples of the extractive extrusion trials were analysed using a deuterated standard to precisely distinguish between the different HBCD intensities for alpha-, beta-, gamma-HBCD-isomers. Later all HBCD-isomers were accumulated to a total HBDC value in wt.-% for better comparison. The results are shown in Table 10.

Table 10: Results of the first campaign

SAMPLES	A-HBCD [WT.-%]	B-HBCD [WT.-%]	Γ-HBCD [WT.-%]	TOTAL HBCD [WT.-%]
CREATOR_C-018 A	1,93	0,38	0,48	2,79
CREATOR_C-018 B	1,85	0,39	0,48	2,72
CREATOR_C-018-AVERAGE	1,89	0,385	0,48	2,755±0,035
CREATOR_C-019 A	1,39	0,34	0,44	2,17
CREATOR_C-019 B	1,41	0,38	0,50	2,29
CREATOR_C-019-AVERAGE	1,40	0,36	0,47	2,23±0,06
CREATOR_C-021 A	1,29	0,34	0,48	2,11
CREATOR_C-021 B	1,39	0,33	0,45	2,17
CREATOR_C-021-AVERAGE	1,34	0,335	0,465	2,14±0,03

The initial results already show promising results as the HBCD content is reduced with the treatment of sc-CO_2 from 2.755±0,035 WT.-% to 2.23±0.06 WT.-%. By the use of acetone, the HBCD further decreases to a value of 2.14±0.03 WT.-%.

3.2.2 EXTRACTIVE EXTRUSION TRIALS – SECOND CAMPAIGN

Based on the analysis of the first campaign described above, the following process modifications were carried out:

- Reduction of process temperature → less degradation, higher process stability
- $T_{process}$= inlet 140 °C, die plate 180 °C
- Polymer throughput extruder: 5 kg/h
- Stripping agents: sc-CO_2 → 3 kg/h; acetone → 150 g/h

Identical to the first campaign, the first sample C-028 is the reference sample which is unmodified (no sc-CO_2 and co-sovlent), but which passes through an identical process to the other following samples. The second sample, C-029, is only treated with sc-CO_2 and the third sample, C-030, is additionally processed with acetone. In Table 11 the experimental set-up of the first campaign is summarized.

Table 11: Experimental set-up – second campaign

TRIAL		EXTRUDER			EXTRACTION		
#	MATERIALS	T (°C) (EXTRUSION ZONE)	SPEED RPM	THROUGHPUT PS KG/H	THROUGHPUT CO2 KG/H	THROUGHPUT ACETONE KG/H	INJECTION PRESSURE GAS/ACETON BAR
CREATOR_028	EPS COMPACTED	170	150	5	0	0	0
CREATOR_029	EPS COMPACTED	170	150	5	3	0	140
CREATOR_030	EPS COMPACTED	170	150	5	3	0,15	120/114

The target was to increase the pressure level during processing to further improve the extraction efficiency which could be successfully realised. The resulting pressure level of the first campaign was 90 bar for CO_2 and

80 bar for acetone. The pressure level of the second campaign increased to 120 bar (CO_2) and 114 bar (acetone).

The resulting samples of the extractive extrusion trials were analysed using a deuterated standard to precisely distinguish between the different HBCD intensities for alpha-, beta-, gamma-HBCD-isomers. Later all HBCD fractions were accumulated to a total HBDC value in wt.-% for better comparison. The results are shown in Table 12.

Table 12: Results of the second campaign

SAMPLES	A-HBCD [WT.-%]	B-HBCD [WT.-%]	Γ-HBCD [WT.-%]	TOTAL HBCD [WT.-%]
CREATOR_C-028 A	1,28	0,33	0,72	-
CREATOR_C-028 B	1,28	0,37	0,73	2,38
CREATOR_C-028-AVERAGE	1,28	0,35	0,725	2,38
CREATOR_C-029 A	1,19	0,36	0,59	2,14
CREATOR_C-029 B	1,25	0,36	0,62	2,23
CREATOR_C-029-AVERAGE	1,40	0,36	0,47	2,185±0,045
CREATOR_C-030 A	1,18	0,34	0,65	2,17
CREATOR_C-030 B	> CALIB.	0,33	0,61	N.N
CREATOR_C-030-AVERAGE	1,18	0,34	0,65	2,17

The results clearly indicate again the reduction of the HBCD values for sample C-029 and sample C-030. This means that both sc-CO_2 alone and the combination of sc-CO_2 and acetone significantly reduce the HBCD contamination of PS. However, the increase in pressure does not indicate a significant reduction of the HBCD values compared to the initial extractive extrusion campaign.

4 CONCLUSION

The first batch trials indicate a reduction of HBCD, but no removal of Br in the mixture was obtained as can be seen in the XRF analysis. A high amount of HBCD can better be removed with acetone, whereas small amounts of HBCD can better be removed with sc-CO_2. This knowledge will be applied to subsequent extruder trials.

The results of the extractive extrusion campaigns show the potential to reduce HBCD from PS melt. Both sc-CO_2 alone and the combination of sc-CO_2 and acetone significantly reduce the HBCD contamination levels. Based on these results, the extractive extrusion will be further optimized and further trials will be carried out.