Recycling of flame retarded waste polystyrene foams (EPS and XPS) to PS granules free of hexabromocyclododecane (HBCDD)

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Keywords: PS foam, EPS, XPS, waste, recycling, HBCDD

Highlights:

- Hexabromocyclododecane (HBCDD) is removed from waste EPS and XPS by solvent based recycling to PS granules
- HBCDD levels in recycled PS are below the low POP content (100 ppm) defined by the EU POP regulation
- The solvent circle is closed and ppm range solvent residues in recycled PS do not alter product properties
- Mechanical properties of recycled PS compare well to virgin PS

Abstract

Expanded and extruded polystyrene (EPS and XPS) belong to the most often used insulation materials and - with respect to this application- both materials have been equipped with the brominated flame retardant hexabromocyclododecane (HBCDD) for more than 50 years. After HBCDD had been identified as a substance of very high concern, it was set under control of the Stockholm Convention and the European REACh legislation. In consequence, the use of HBCDD in insulation materials is
Currently phased out and waste insulation material made of HBCDD equipped EPS or XPS cannot further be subjected to state-of-the-art mechanical recycling.

However, as the majority of the formerly produced HBCDD equipped EPS and XPS is still in use as insulation material, more sophisticated recycling approaches are currently investigated.

This study investigates a solvent based recycling process, which dissolves polystyrene from insulation waste and eliminates not only insoluble waste components but also co-dissolved HBCDD. The study investigates the efficiency of HBCDD removal as well as mechanical properties of recycled PS produced by this process.

Results indicate a save separation from inorganic waste and other non-target polymers as well as an extraction of more than 99.6% of initially present HBCDD. Mechanical properties of recycled PS are in the expected range of virgin general purpose PS as long as the separation of residual solvents from the recycled polymer is sufficient, i.e. residual solvent content < 0.1 %.
Introduction

Products made of expanded polystyrene (EPS) and extruded polystyrene (XPS) are well established in the world-wide construction and packaging markets. Stability and low specific weight qualify both materials for insulation applications as well as usage as packaging material for consumer goods and food. EPS is also part of external thermal insulation composite systems (ETICS), which are used as convenient insulation material in construction and refurbishment of buildings. The association of European Manufacturers of Expanded Polystyrene (EUMEPS) reported in 2011 an annual production of EPS in the packaging sector of 1.2 Mio tons in Asia and 0.34 Mio tons in Europe. In contrast, the EPS market in construction applications accounts for 1.2 Mio tons per anno respectively in both regions, Europe and Asia [1].

End-of-life treatment of EPS and XPS from packaging is established, since waste from these applications emerges shortly after usage and is well covered by take-back systems for packaging waste. In contrast, only small streams of waste XPS and EPS are reported from construction waste. This is due to two reasons: First, most insulation panels are still in place and second, PS is mostly not separated from mixed demolition waste and not subjected to PS recycling.

In general, PS foams are established input fractions of PS recycling activities in industrial scale [2]. EPS recycling targets mostly at waste EPS packaging. This is performed by mechanical processes, mainly, including, compression, grinding and re-compounding. EPS from construction waste, however, was often used for production of light-weight concrete and render [3,4,5]. Because of numerous contaminants recycling technologies become more complex when post-consumer waste is processed. Contaminants include, mortar and glue, adhesive tape, food residues.

A major problem of EPX and XPS recycling, however, is the transport of the voluminous and extremely lightweight material to the respective treatment plants. Therefore, compaction of the waste material is state of the art. Seo and Hwang have reviewed suitable technologies, including moulding, mechanical compaction and solvent application [6]. If solvents are involved, further treatment is performed by solvent based polymer recycling technologies [7,8,9,10].

Since 2014/2015 there is another obstacle to recycling of XPS and EPS from construction waste. Due to regulatory requirements, XPS and EPS in construction application have to be equipped with flame retardants. In the past, hexabromocyclododecane (HBCDD) was the flame retardant of choice for EPS and XPS with global market shares higher than 95%. In 2008 the European Union identified HBCDD as a Substance of Very High Concern (SVHC) due to its PBT properties (persistent, bioaccumulative, toxic), and it was included in Annex XIV of the REACH Regulation in 2011 [11]. The production and application of HBCDD in PS foams in the EU is only possible if an application for an authorisation has been made by August 2014 and a temporary authorization has been granted by the European Chemicals Agency (ECHA) and the European Commission. On 9 May 2013 HBCD has been added to Annex A (Elimination) of the list of persistent organic pollutants (POP) of the Stockholm Convention. The decision means that the production and use of HBCD will be banned. A time limited exemption can be applied for, for production and use of PS foams for buildings.

In reaction to these legal developments a special polymeric brominated flame retardant (PolyFR) has been developed in order to replace HBCD in PS foam for building and construction applications [12]. However, in the coming twenty to fifty years, waste EPS and XPS from construction and demolition waste will contain significant amounts of HBCDD.
According to current legislation, destruction of HBCDD containing waste is the only accepted way of treatment [13, 14]. However, an alternative and probably more sustainable approach would be a separation of HBCDD from the polystyrene matrix and to recover flame retardant free polystyrene for new applications. Separated flame retardants may serve as a source for secondary bromine if it is in a suitable state for the respective recovery technology.

Separation of brominated flame retardant additives from polystyrene has been achieved by the CreaSolv® process as reported earlier [15]. This technology is one of the above mentioned solvent based recovery approaches and applies secure solvent formulations to dissolve a target polymer (e.g. PS or EPS) from a waste stream and separates it from undissolved matter. Further extractive cleaning, however, enables the separation of brominated flame retardants from the matrix and produces – after solvent recovery – granules of the purified target polymer. In 2004, the CreaSolv® process has been successfully applied to waste EPS however, removal of HBCDD has not been an issue these days and has not been investigated in detail. In addition, performance of the CreaSolv® process has improved thanks to two recently finished research projects, PolyRessource and PolySOLVE [16, 17]. Project outcomes were an optimized technology on extractive cleaning on the one hand and an improved solvent recovery approach.

The aim of this paper is to present current experimental data on the recycling of HBCDD containing EPS. A focus is set on the removal of HBCDD, both in laboratory and small technical scale. In addition, the mechanical properties of recycled PS are determined and discussed, in order to highlight whether an improved CreaSolv® process resulted in improved properties recyclates.

2 Material and Methods

2.1 Materials

2.1.1 PS foams

PS foams from demolition waste were sampled directly at a demolition site. Plaster was removed directly at the site, but the material still contained residues of glue and mortar. Post-industrial XPS waste was provided by Sunpor, a European EPS and XPS producer. Stryrolution PS 156 F, a virgin PS type for production of PS foams, was purchased from Biesterfeld Plastic GmbH. PS foams as well as their contaminants and additives were listed in Table 1.

Table 1: Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>Origin</th>
<th>Applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste EPS/XPS</td>
<td>Foams from demolition waste</td>
<td>Austria</td>
<td>Laboratory scale tests</td>
</tr>
<tr>
<td>XPS Waste</td>
<td>Post-industrial XPS scrap from extrusion provided by Sunpor</td>
<td>Austria</td>
<td>Laboratory and small technical scale</td>
</tr>
<tr>
<td>Virgin GPPS</td>
<td>Stryrolution F156, which can be used for production of XPS</td>
<td>Germany</td>
<td>small technical scale</td>
</tr>
</tbody>
</table>
2.1.2 Solvents

For solvent based recycling two solvent formulations were purchased from CreaCycle GmbH, Grevenbroich, Germany: Creasolv® PS as solvent for PS foams and Creasolv® PSF as an anti-solvent. Creasolv® is a registered trademark of the CreaCycle GmbH, Grevenbroich.

For analytical issues per analysis grades of tetrahydrofuran, ethanol, and acetone were purchased by Merck (Darmstadt, Germany).

2.2 Methods

2.2.1 General Recycling Approach

The CreaSolv® process recovers PS from PS foam containing wastes. It makes use of proprietary CreaSolv® PS formulations, which are not considered as dangerous according to EU Directive 1272/2008 (CLP/GHS). In a dissolution unit, the waste is treated with the solvent formulation and dissolves PS foams, EPS and XPS. The PS solution is then cleaned from insoluble waste components (dirt, cement, glue, metals, foreign polymers etc.) in a mechanical solid-liquid separator. Insoluble material is dried to recover the solvent for further reuse within the process. The POP listed brominated flame retardant HBCDD, however, cannot be removed from PS mechanically and requires an extractive purification step. The extractive cleaning unit separates dissolved HBCDD from a precipitated PS gel. Solvents incorporated in the PS gel are removed in a polymer drying unit. This allows recovering more than 99.5% of the solvent and produces granules of recycled PS. These may be used for production of GPPS, XPS or EPS. Solvents are recovered from HBCDD extracts by a solvent recovery unit and reused within the process. The HBCD fraction is considered for bromine recovery, whereas the insoluble material is treated as “POP free” demolition waste.

2.2.2 Laboratory scale investigations

10-300 g samples of post-industrial and post-consumer waste EPS and XPS (samples B and C) were treated with CreaSolv® PS. In laboratory scale undissolved matter like concrete and mortar was separated by sedimentation and coarse filtration.

HBCDD was eliminated by extractive cleaning. Therefore, an anti-solvent was added to the filtered polymer solution, resulting in a polymer gel and an extract phase. The latter was expected to contain a major portion of the HBCDD separated from the gel. In order to increase the purification level, extractive cleaning was performed step wise. In each purification step, weights of gel and extract phase were recorded and sub-samples of both phases were subjected to XRF analysis.
Solvent dry PS granules were produced from extraction cleaned polymer gels by drying the material in a vacuum oven for 4 hours. Solvent residues were subsequently removed by laboratory scale vacuum extrusion.

2.2.3 Small technical operations

Using the small-technical CreaSolv® plant at the Fraunhofer Institute IVV a 14 kg PS sample was produced from post-industrial waste XPS (Sample B). The waste material was coarsely crushed and dissolved in CreaSolv® PS using a stirred and jacket heated 100 L reactor. After dissolution XPS was filtered through a 100 µm filter and subjected to a multi-step extraction for removal of HBCDD.

Filtered and extracted gels were subsequently separated from solvents and anti-solvents using a stirred jacket-heated drum. Vacuum was applied by a vacuum pump and solvent vapors were condensed and trapped. Intermediate PS products were discharged from the vessel volume and analysed for its residual solvent content.

Final drying was performed at an external partner on a specialized extrusion line. The extrusion line has a capacity of 40kg/h. Compared to the smaller scale drying applied in the European PolySOLVE project (3kg/h), this aggregate provided a superior drying efficiency, due to an improved temperature profile and screw design of the degassing line.

2.2.4 Material testing

Differential Scanning Calorimetry (DSC) was used to investigate the glass transition temperature. The measurement was carried out on a Mettler Toledo DSC 821 instrument and temperature was raised from 25°C to 140°C at a heating rate of 10 °C/min.

Determination of molecular weights (Mw) was based on DIN 55672-1 using gel permeation chromatography (GPC). Before measurement the PS samples were dissolved in THF (2500 ppm) and filtered through a 0.2 µm PTFE syringe filters. The measurement was carried out by an ASI-100 automated sample injector (Dionex), a high precision pump (Model 300, Gynkotek), a degasser (ERC-3612, Erma), a column oven (Spark Holland Mistral) using 2 GPC columns (5 µm, 8*300 SDV, linear M) at 40°C with THF as mobile phase. Detection was performed by an RI detector (UVD 340S, Gynkotek). For calibration and analysis, narrowly distributed PS standards dissolved in THF were used.

The determination of Melt Flow Indices (MFI) was carried out according to ISO 1133 by using a CEAST modular MFI at 200°C and 5 kg test weight. After conditioning samples according to DIN EN ISO 291
tensile tests were performed according to DIN EN ISO 527-2. Testing of the Charpy impact strength followed DIN EN ISO 179-1.

Intermediate and final products were analyzed for residual solvent amounts by subjecting samples to head-space gas chromatography coupled to a flame ionization detector (HS-GC-FID). Quantification was based on the principle of multiple headspace injection.

2.2.5 Analysis of bromine and HBCDD

X-ray fluorescence analysis (XRF): XRF was used for bromine analysis using an energy dispersive XRF desktop instrument (Spectro, SpectroLab 2000). Extracts and polymer gels were filled into XRF cups (LGC, Germany) sealed with Prolene® films. Both types of samples were placed on the XRF autosampler and bromine was analyzed using the standard calibration of the XRF system.

Residual levels of HBCDD were quantified in final products and input samples by LC-MS: Recycled PS was dissolved in tetrahydrofurane (10 wt%) and precipitated by addition of a fivefold amount of EtOH. Supernatants were separated from the PS gels and subjected to LC/MS analysis after passing a 0.45 μm PTFE syringe filter. LC/MS was performed on a QuattroLC, Waters.

3. Results and Discussion

3.1 Laboratory scale investigations

3.1.1 Dissolution and mechanical cleaning

In agreement with Patent EP 1438351 B1 dissolution of EPS and XPS was successfully performed by a specific CreaSolv® solvent formulation applied far below its flash point. Therefore, the liquid is safely applicable for dissolution in industrial scale recycling plants but could also be used in outdoor environments like demolition sites.

Dissolved EPS and XPS were cleaned from undissolved matter by mechanical means first. The amount of undissolved matter strongly depends on the investigated samples. Whereas waste EPS and XPS panels from construction sites of new buildings are mostly free from undissolved matter (e.g. Sample B), dissolved post-consumer EPS from waste external thermal insulation composite systems (ETICS) contained mortar, glue and fabric (Sample C). EPS solutions from ETICS were cleaned by sedimentation and subsequent filtration. Undissolved material did not interact with the CreaSolv® liquid. A production scale operation would require a surface drying and solvent recovery unit to recycle this amount of liquid.
3.1.3 Extractive cleaning

HBCDD is co-dissolved by the CreaSolv® formulation liquid and cannot be separated from PS solutions by mechanical means. Thus, an extractive cleaning approach was chosen, which bases on the principle of dissolution and precipitation. An anti-solvent was added to the mechanically cleaned PS solutions leading to a two-phase system comprising of the polystyrene gel and the extract.

In laboratory scale trials the initial concentration of dissolved PS was varied over a wide range. After the first precipitation each PS gel was extracted several times. To understand the cleaning efficiency, bromine concentrations were determined in extract and polystyrene gel by XRF. As HBCDD was assumed to be the only source of bromine in the investigated material, bromine is evaluated as indicator for HBCDD. HBCDD levels were calculated from measured bromine levels basing on the assumption of 75% bromine in HBCDD. As the distribution of HBCDD between both phases was shown to be constant, this parameter allowed setting-up a calculation model for a multistep cleaning procedure. As a result, the model could be used to predict the required number of successive extraction steps for a given start concentration of HBCDD in order to reduce the HBCDD by 99.6-99.8% to a level below 100 ppm (Table 2).

Table 2: HBCDD levels of laboratory scale products

<table>
<thead>
<tr>
<th>Waste</th>
<th>Starting level [ppm]</th>
<th>Product concentration [ppm]</th>
<th>Purification [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste EPS/XPS</td>
<td>16000</td>
<td>37</td>
<td>99.8%</td>
</tr>
<tr>
<td>XPS Scrap</td>
<td>15000</td>
<td>56</td>
<td>99.6%</td>
</tr>
</tbody>
</table>

3.2 Small technical results

3.2.1 Dissolution and mechanical cleaning

The issue of dissolving PS or PS foams differs significantly in terms of technical application of the CreaSolv® formulation. However, both inputs could be processed to polystyrene solutions.

Waste composition is the major factor defining the required mechanical cleaning devices for dissolved PS, which again based on the principle of sedimentation and filtration.

3.2.2 Elimination of HBCDD

Extractive cleaning was chosen for demonstration in small technical scale and reduced HBCDD levels in extracted PS gels successively, as measured by XRF. Again computed and measured levels in extracts and gels were in line. This indicates that laboratory scale investigations of the extraction process were scalable to small technical scale with sufficient precision.
The PS gel after extraction reached a level of 47 ppm HBCDD, based on XRF fluorescence analysis. This refers to a purification of 99.7% and states the purification levels reached in lab scale.

3.2.3 Product drying and solvent recovery

Product drying is necessary to separate solvent from recycled PS and to recover the solvent for further use within the process. Heat and vacuum were applied for this purpose. In our trials with virgin PS we reached a final solvent residue level of 800 ppm. Recycled products from waste XPS achieved even 600 ppm as residual solvent content.

Solvents were also recovered from extracts of the HBCDD removal steps. The polymer content in these phases is rather low and allows a much faster drying. As the interface to a subsequent bromine recovery unit had not been defined in detail yet, we stopped the drying process at a dry matter content of 30-50%. Further drying would process the viscous liquid by-product to a much more solid product.

3.4 Mechanical product properties

Product properties of laboratory scale products are listed in Table 3, properties of small-technical productions are presented in Table 4.

The glass transition temperature of virgin PS is expected in the range of 100-105°C. Measurements of incompletely dried PS exhibit much lower Tg levels, whereas both completely dried samples show glass transition temperatures slightly above 100°C.

Recycled PS from virgin PS with an MFI of 35.6 g/10min exhibits an MFI of 72.9 g/10min after incomplete and almost the level of virgin PS after final drying (34.2 g/10min). The melt flow index of the final product produced from waste XPS is slightly lower.

The molecular weight of PS is preserved during and after the recycling process. The deviations of the measured results are within the 10 % measurement tolerance. This result is supported by the MFI value, which exhibits also no significant decrease between input material and recycled PS. The melt viscosity is highly dependent on the molecular weight of the plastic.

An optimized setup of screw and temperature profiles increased the performance of the extrusion line resulting in a residual solvent content of less than 1000 ppm. Due to the low residual solvent content a glass transition temperature (Tg) of 103 °C was obtained in final products, which corresponds well to the Tg of virgin PS (Input material).
In addition, neither MFI, nor molecular weight analysis or Charpy impact testing showed a significant deterioration of parameters compared to the virgin material (input material). The results indicate the importance of achieving a residual solvent content of less than 1000 ppm to generate a high quality recycled PS. However, if this requirement is fulfilled, recycled PS reaches properties of virgin PS.

Table 3: Chemical properties of laboratory scale products compared to input

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mw</th>
<th>PD</th>
<th>Residual solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimension</td>
<td>g/Mol</td>
<td>Dalton</td>
<td>[%]</td>
</tr>
<tr>
<td>Input</td>
<td>176.229</td>
<td>3.12</td>
<td>-</td>
</tr>
<tr>
<td>Input, crushed</td>
<td>178.481</td>
<td>2.83</td>
<td>-</td>
</tr>
<tr>
<td>Intermediate PS gel</td>
<td>195.802</td>
<td>1.89</td>
<td>approx. 50</td>
</tr>
<tr>
<td>Dried intermediate PS product</td>
<td>195.892</td>
<td>1.86</td>
<td>2</td>
</tr>
<tr>
<td>Vacuum dried PS product</td>
<td>196.007</td>
<td>2.17</td>
<td>0.262</td>
</tr>
</tbody>
</table>

Table 4: Chemical properties of recycled PS from XPS compared to virgin GPPS and recycled GPPS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg [°C]</th>
<th>MFI [g/10min]</th>
<th>Solvent content [ppm]</th>
<th>Molecular weight (Mw) [g/mol]</th>
<th>Charpy Impact test [kJm-2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin GPPS (Styrolution PS 156 F)</td>
<td>102.5</td>
<td>35.6</td>
<td>n.d.</td>
<td>146002</td>
<td>6.16 ± 1.02</td>
</tr>
<tr>
<td>Intermediate recyclate from GPPS (~96% dry matter)</td>
<td>55.1</td>
<td>72.9</td>
<td>40000</td>
<td>144943</td>
<td></td>
</tr>
<tr>
<td>Recycled GPPS</td>
<td>103.0</td>
<td>34.2</td>
<td>800</td>
<td>141053</td>
<td>6.46 ± 0.31</td>
</tr>
<tr>
<td>XPS scrap</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>175533</td>
<td></td>
</tr>
<tr>
<td>Intermediate recyclate from from XPS (~98% dry matter)</td>
<td>71.4</td>
<td>n.d.</td>
<td>20000</td>
<td>177721</td>
<td></td>
</tr>
<tr>
<td>Recycled PS from XPS</td>
<td>105.9</td>
<td>24.9</td>
<td>600</td>
<td>170236</td>
<td></td>
</tr>
</tbody>
</table>
4 Conclusions

4.1 Technical readiness level of the CreaSolv® Technology

The development of a suitable PS foam recycling process was performed over a rather long period as many technical challenges had to be addressed. The general principle of dissolving PS from EPS/XPS waste streams and extractive elimination of HBCDD has already been developed in 2004. However, process cost and final product quality were not good enough for industrial upscale at that time. Further process developments were achieved by using different PS sources like waste electric and electronic equipment (WEEE) [15]. The final technical issue, however, was a robust and affordable drying technique, which was not available on the market and had to be developed from scratch until 2012 [16]. This new drying concept was then tested in the European PolySOLVE project. In this project, green solvents from natural origin were used instead of CreaSolv® formulations. Final products from PolySOLVE demonstration trials however, failed to comply with required product qualities, mainly due to an incomplete drying. It remained unclear whether this was caused by specific solvent-polymer interactions or by technical issues.

Drying trials reported in this study, however, applied a further optimized drying technique, especially a more sophisticated extrusion line. This concept managed to reduce the residual solvent amount in final products significantly.

After all, every process step of the CreaSolv® concept has been developed in laboratory scale and has successfully been upscaled to small technical scale. According to the concept of technical readiness we notify a TR level of 5-6. Thus, installation and operation of a pilot prototype would be the next logic steps in the further evaluation and demonstration of the CreaSolv® process.

4.2 Managing waste PS foams with CreaSolv® Technology

Firstly, material recycling from PS foams will always compete to alternative treatment options, mainly incineration. Secondly however, incineration or a CreaSolv® process will always be just a part of the solution. Prior to treatment, HBCDD equipped PS foams have to be collected and transported from the places of waste origin, i.e. widely dispersed demolition and refurbishment sites. The conventional way of collection would include a coarse shredding, a separation of foreign materials (cement, mortar, glue, etc.) and a compression of foams to increase the waste density. An innovative
approach may involve a collection in solvent tanks followed by separation of foreign materials by solid liquid separation. This would allow a separation of PS and HBCDD from mineral scrap (free of HBCDD) outside of the CreaSolv® plant. Such solvent tanks would collect EPS from regional collection sites as long until viscosity of the PS solution reaches a defined level. Then the PS solution would be delivered to and processes at a central CreaSolv® plant.

Downstream from the CreaSolv® process bromine rich products have to be treated. As an alternative to safe disposal in a hazardous waste incineration plant we suggest to apply this fraction to a bromine recovery unit, as this fraction does not contain catalytically active (heavy) metals like copper. Finally, recovered bromine may be used as a resource for new polymeric brominated flame retardants, PolyFR, which are applied to EPS and XPS these days.

The scheme of recycling uses waste PS foams and produces two important products for the production of new XPS, i.e. recycled PS as a substitute for general purpose PS with extended molecular length and bromine as a source of the polymeric brominated flame retardant PolyFR. The suggested approach is therefore a promising example of the sustainable concept of a circular economy.

5 References

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