Sc-CO₂ extraction of brominated flame retardants from plastic materials coming from waste electrical and electronic equipment prior to recycling

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The valorisation of plastics coming from waste electrical and electronic equipment (WEEE) and containing brominated flame retardants (BFR) is restricted by the regulation $2019/1021/EU^1$. Indeed, some BFR, such as some polybromodiphenylethers (PBDE) are prohibited because of their persistent organic pollutant (POP) property. Therefore, plastic materials containing these substances can be recycled only if their concentrations in BFR recognized as persistent organic pollutants (POPs) are inferior to the regulation limits. The objective of this work is to study the ability of supercritical CO₂ (*sc*-CO₂) to remove BFR from real WEEE-based plastic materials before mechanical recycling.

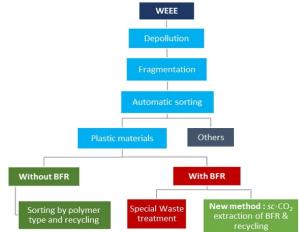


Figure 1 : WEEE dismantling and sorting.

In the present work, experiments were performed on a post-consumer WEEE-derived ABS in which the concentration in BFR recognized as POPs was found to be 4 times higher than the regulation limit. The average BFR composition in the polymer was about 88% of tetrabromobisphenol A (TBBPA) and 11% of PBDE as determined by gas chromatography coupled with mass spectrometry (GC-MS) analysis.

The *sc*-CO₂ process parameters such as temperature (40 to 100°C), pressure (500 and 700 bars), granulometry of sample (< 500 μ m, 1-2 mm and 2-4 mm) and the addition of a co-solvent (ethanol or diethyl ether) were studied. For each parameter set, the extract and the polymer material were characterized to determine the efficiency of BFR extraction and the effect of the *sc*-CO₂ process on the polymer matrix. The extraction process performed on < 500 μ m particle size sample at 40°C and 500 bars, during 6h, using ethanol as a co-solvent allowed to remove 43.5 ± 0,9% of bromine, which was the maximum extraction rate obtained. The results showed that the extraction of TBBPA was limited by diffusion while the extraction of PBDE was rather limited by its solubility in *sc*-CO₂. Finally, *sc*-CO₂ process was found to be a promising pre-treatment technique prior to mechanical recycling as no degradation effect on the polymer matrix was measured by Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Size Exclusion Chromatography (SEC) but the PBDE extraction rate needs to be enhanced to satisfy the regulation.

This work is a proof of concept which allows to validate the technical feasibility of the BFR extraction from a polymer matrix on a laboratory scale and provides elements to understand the mechanisms

(1) 2019/1021/EU, 2019. Regulation (EU) 2019/1021 of the European Parliament and of the Council on persistent organic pollutants.

involved. In future studies, the extraction rate will be optimized and studies on larger volumes will be performed in order to extrapolate the process to an industrial scale.

^{(1) 2019/1021/}EU, 2019. Regulation (EU) 2019/1021 of the European Parliament and of the Council on persistent organic pollutants.