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学 位 記 番 号	博士（環境科学）
学 位 授 与 年 月 日	環（博）第104号
学位授与の根拠法規	平成 27 年 9 月 25 日
研究科，専攻の名称	学位規則第 4 条第 1 項
学 位 論 文 題 目	東北大学大学院環境科学研究科（博士課程）環境科学専攻
指 導 教 員	Development of New Processes for the Dehalogenation and Segregation of Halogen-containing Polymers for their Recycling (ハロゲン含有ポリマーのリサイクルに向けた脱ハロゲン化および分離プロセスの開発)
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論 文 内 容 要 旨

Halogen containing plastics are perhaps the most challenging to safely dispose of or recycle. Processing halogenated plastic waste implies additional economic burdens from the facility's maintenance and repair, as well as the special measures needed to control the emission of dangerous halogenated organic by-products [1]. However, the need to effectively reutilize this plastic waste is not only due to the scarcity of petrochemical resources; it is also a matter concerning the conservation of the environment and the prolonged use of land. This research focuses on two of the aforementioned halogenated plastics, namely poly(vinyl chloride) (PVC) and brominated flame retardant-containing high impact polystyrene (HIPS), and the dehalogenation pretreatments for their recycling or safe disposal.

STEAM-ASSISTED DEHYDROCHLORINATION OF PVC MATERIALS: In this study, PVC resin and flexible PVC (FPVC) containing around 50 wt% of diisononyl phthalate (DINP) plasticizer were subjected to a steam-assisted thermal treatment for

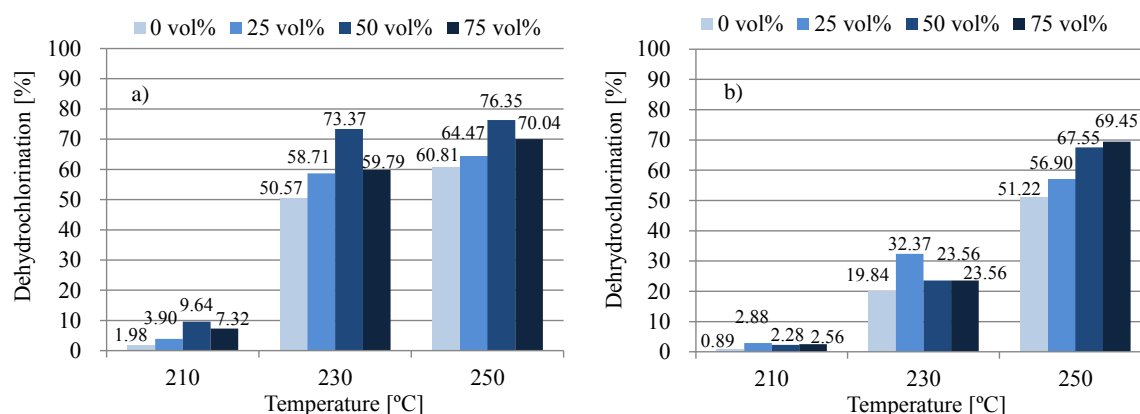


Figure 1. Dehydrochlorination ratio as a function of temperature and steam concentration for a) PVC resin and b) flexible PVC.

their dehydrochlorination. Various steam concentration were tested and compared with dry thermal treatment results in terms of the effect of steam concentration on dehydrochlorination ratio, solid residue composition, and reaction kinetics. The use of steam helped to overcome the poor and inhomogeneous heat transfer and improve dehydrochlorination. The most effective steam concentration was 50 vol%, with most of the reaction occurring between 15 and 60 min after reaching the reaction temperature. The addition of steam at 250 °C increased the maximum limit of dehydrochlorination by about 15 % for both sample types compared to experiments without steam in N₂ atmosphere (Figure 1) [2]. The steam assisted thermal dechlorination reaction was determined to be apparent first-order with an activation energy of 120 kJ mol⁻¹, which is similar to the case without steam. However, the pre-exponential factor was 68 % higher in the case of steam, suggesting a physical effect such as increased mass and heat transfer rather than a chemical one. This assumption is supported by dimensional flow parameters such as the Prandtl, Schmidt and Peclet numbers, which favor a steam flow over a He one in terms of transfer.

INTERACTION BETWEEN PLASTICIZER AND PVC DEGRADATION PRODUCTS IN THE STEAM-ASSISTED THERMAL TREATMENT: Thermal degradation of FPVC was performed under atm. pressure in the temperature range of 190 to 250 °C both in the presence and absence of steam. In order to compare the effects of temperature and steam on the degradation of FPVC, experiments using only PVC resin or dioctyl phthalate (DOP) plasticizer were also performed under the same

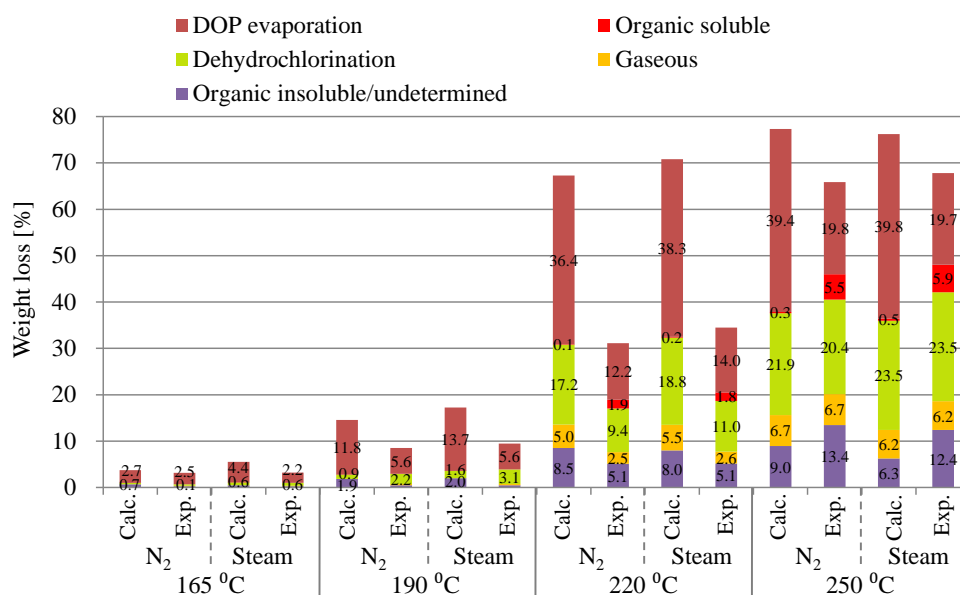


Figure 2. Comparison between calculated and experimental results for the total weight loss and weight loss contributions of flexible poly(vinyl chloride) (FPVC) at various temperatures in the presence or absence of steam.

conditions. Although the FPVC used was composed almost exclusively of PVC and DOP (around 65 and 45 wt%, respectively), the weight loss behavior, extent of dehydrochlorination, plasticizer evaporation, and degradation products were significantly different from those from the experiments of both components independently (Figure 2). In the DOP-only experiments hydrolysis of the plasticizer was not observed even when steam was present. However, in experiments using FPVC hydrolysis was observed, as evidenced by the predominant formation of phthalic anhydride, 3-chloromethylheptane, and 2-ethylhexanol. Thus, it is most likely that plasticizer was acid hydrolyzed by the HCl released from the dehydrochlorination of the PVC component. These results show that the thermal decomposition of FPVC cannot be assumed

to be just the combination of the decomposition of its components independently; interactions between PVC and plasticizer are relevant and cannot be overlooked.

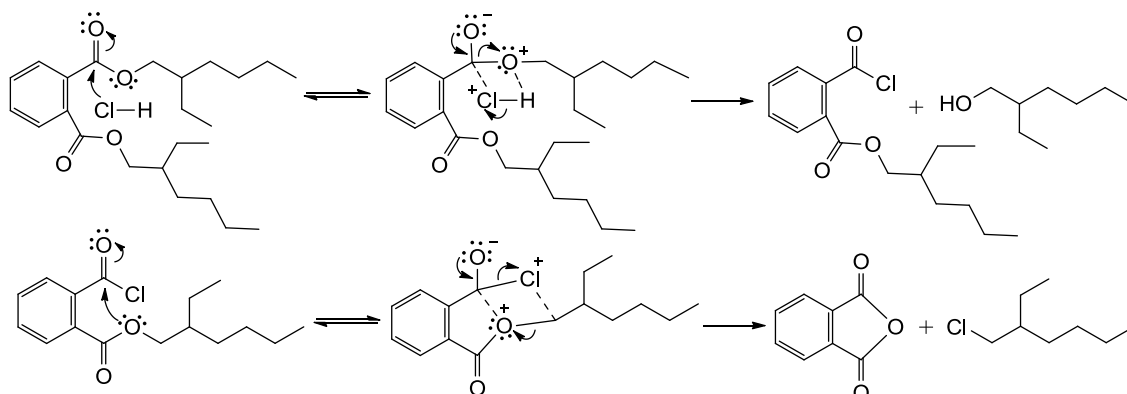


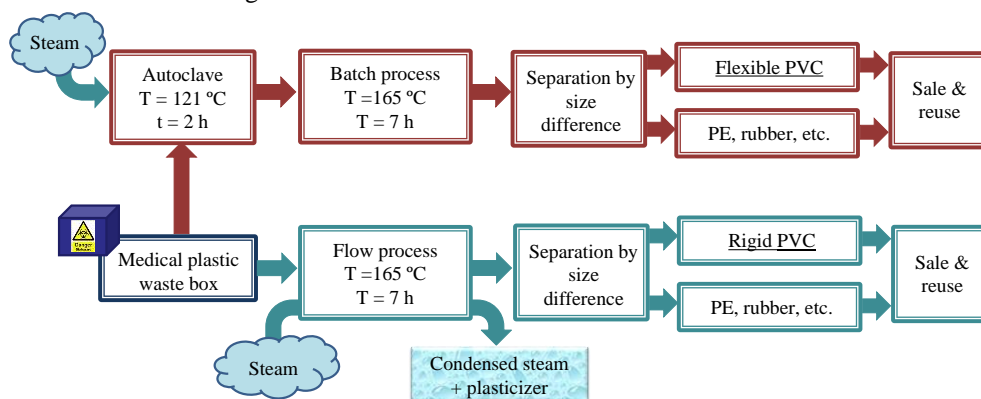
Figure 3. Reaction of HCl resultant from the dehydrochlorination of poly(vinyl chloride) (PVC) with the dioctyl phthalate (DOP) plasticizer.

SELECTIVE FLEXIBLE PVC STEAM-ASSISTED MECHANICAL GRINDING: This research aimed to develop a novel process for



Figure 4. Mixture of plastic tubes a) before and b) after processing in Johnson boiler-ball mill. FPVC tubes are originally transparent and PE tubes are white and green.

the recycling pre-treatment of medical use FPVC waste. The concept is to combine steam thermal treatment and ball milling in order to achieve simultaneous sterilization and selective size reduction of the FPVC component in a mixture of medical waste plastics. In order to exert enough force to crush the FPVC tube samples, an industrial scale rotary kiln adapted to work as a ball mill with a heated steam inlet was used. It was



important to determine processing conditions to recover the FPVC without dehydrochlorination for two reasons. The first reason is that only non-degraded material is acceptable for mechanic recycling.

Figure 5. Flow diagram of proposed adaptable treatment for the simultaneous sterilization and separation of medical use plastic waste.

Secondly, the HCl released by dehydrochlorination would corrode the steel

reactor and pipes, causing costly damage to the equipment. Taking these factors into consideration optimal operating

conditions were experimentally determined. It was found that selective crushing of FPVC occurred only when the combined effect of the three parameters of temperature, steam, and shock from milling were present. The best processing conditions were determined to be 165 °C, 6 h, 20 rpm, 17 kg h⁻¹ steam, and 10 kg of aluminum balls. Selective size reduction of only FPVC tubes was achieved without degradation of the FPVC, allowing both the easy separation and possibility to reuse the material. Plasticizer solvent extraction and autoclaving were tested as pretreatments. It was found that extracting the plasticizer caused the PVC tubes to become too hard to be able to ground by the ball mill. On the other hand, the autoclave pretreatment showed that it is possible to execute the selective ball mill size reduction of flexible PVC tubes either as a flow type process (feeding steam continuously into the reactor) or as a batch process (autoclave pretreatment and no steam feed into reactor when milling). In the case of batch processing, the PVC is ground just as in the base flow process, but plasticizer remains in the sample allowing the recovery of flexible PVC.

BALL MILL ASSISTED DEBROMINATION OF FLAME RETARDANT-CONTAINING HIPS IN ETHYLENE GLYCOL ALKALINE SOLUTION: This research provided efficient removal of a brominated flame retardant from HIPS using NaOH/ethylene glycol

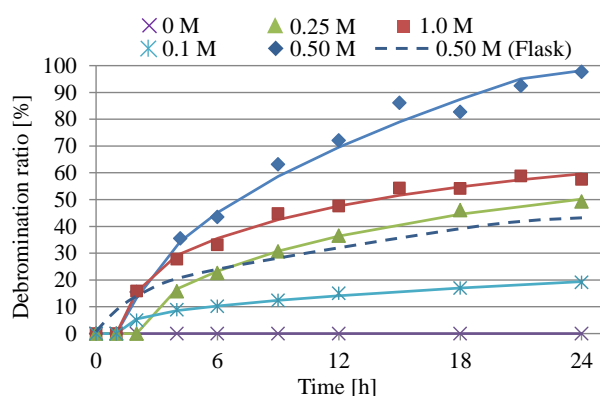


Figure 4. Debromination of HIPS-DBDPE samples at various NaOH concentrations under constant temperature of 190 °C ball mill reactor.

thermal properties of the recovered polymer. HPLC-MS analysis of the EG solution showed that bromine was substituted partly by hydroxyl groups and partly by hydrogen.

solution (NaOH_(EG)) under mild conditions between 150 and 190 °C in both a stirred flask and a ball mill reactor, based on the success of the dechlorination of PVC in a NaOH_(EG) [3]. Decabromodiphenyl ethane (DBDPE) was chosen as the brominated flame. The debromination of DBDPE-containing HIPS in NaOH_(EG) at 190 °C resulted in high debromination ratios of near 100 % (Figure 6) [4]. In particular, ball milling was proven to be a mild method appropriate for the removal of bromine from a polymer matrix. The residual polymer might have been cross-linked through the DBDPE backbone. Other signs of degradation were not observed. TGA revealed excellent

SYNTHESIS AND CONCLUSIONS: Various pretreatments for the recycling or safe disposal of halogen-containing polymers PVC and flame-retarded HIPS were investigated. The focus has been the use of steam under atmospheric pressure, as well as grinding using ball milling. The processes were observed to have potential for real application, as shown by the research conducted for the disposal of medical used plastic waste. However, in order to consider these processes as a means for disposal or recycling pretreatment the toxicity of the resulting components should be clarified and the actual reusability of the solid residues obtained must be tested.

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論文審査結果の要旨及びその担当者

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論文題目	Development of New Processes for the Dehalogenation and Segregation of Halogen-containing Polymers for their Recycling (ハロゲン含有ポリマーのリサイクルに向けた脱ハロゲン化および分離プロセスの開発)
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論文審査結果の要旨

現在、ポリ塩化ビニル (poly(vinyl chloride), PVC) および耐衝撃性ポリスチレン (high impact polystyrene, HIPS) 等ハロゲン含有ポリマーの廃棄物に対する、安全かつ効果的なリサイクル手法は未だ確立していない。既存のハロゲン非含有ポリマーに有効な熱化学処理をハロゲン含有ポリマーに適用した場合、処理設備の腐食の原因となるハロゲン化水素の生成、および環境や人間に有害なハロゲン化有機化合物を生成することが明らかとなっている。本論文は、ハロゲン含有ポリマー廃棄物を安全かつ効果的にリサイクル可能とする、脱ハロゲン化プロセスの開発を行い、その成果をまとめたものである。

第1章は緒論であり、上述のような研究の背景および目的を述べた。

第2章では、PVC 樹脂と可塑剤含有軟質 PVC の水蒸気添加による脱塩素プロセスを検討した。水蒸気存在によって、脱塩素率と脱塩素反応速度定数が増加することを見出した。PVC 材料の脱塩素反応に及ぼす温度および水蒸気量の影響を明らかにした。

第3章では、前章で検討した PVC の水蒸気添加による脱塩素プロセスにおける可塑剤の影響に着目し、検討した。その結果、PVC から生じる HCl が、揮発した可塑剤 (ジオクチルフタレート (DOP)) の加水分解を促進するメカニズムを明らかにした。

第4章では、医療系プラスチックの約40%が軟質 PVC である、医療系プラスチック廃棄物に着目し検討を行った。本章では、第2章および第3章とは異なり、PVC の脱塩化水素を抑制しつつ PVC 樹脂のみを選択的に微粉化することを目的とした。ボールミルを用いた粉化試験において、反応温度、水蒸気量、および反応時間などの影響を検討し、軟質 PVC の選択的な微粉化に適した反応条件を明らかにした。さらに、PVC のみが粉化される性質を利用し、PVC と他のプラスチックがそれぞれ分離回収可能であることを見出した。

第5章では、第4章のボールミル試験および第2章の脱塩素の知見を応用し、ボールミルを用いた NaOH/エチレングリコール溶液による、臭素系難燃剤含有 HIPS の脱臭素プロセスを検討した。ボールミルを組み合わせることで、脱臭素率および脱臭素速度を大幅に向上することに成功した。よって、効果的な脱臭素を可能とする反応条件を明らかにし、臭素系難燃剤含有プラスチック廃棄物への応用可能性を見出した。

第6章は本研究の総括であり、得られた成果のまとめ、本研究の社会的および学術的意義について述べた。

以上、本論文は、安全かつ効果的な脱ハロゲン化処理が可能であることを明らかにし、これまで効果的なリサイクル手法が確立していなかったハロゲン含有ポリマーのリサイクルの可能性を見出した。本研究が、リサイクル手法の一つとしてハロゲン含有ポリマー廃棄物の処理手法の可能性を拓き、将来的なハロゲン含有ポリマーのリサイクルの基盤技術として有益となることが期待される。

よって、本論文は博士(環境科学)の学位論文として合格と認める。