氏　　名	NONA MERRY MERPATI MITAN
授与した学位	博　士
専攻分野の名称	学　術
学位授与番号	博甲第３８９９号
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学位授与の要件	自然科学研究科　機能分子化学専攻 （学位規則第５条第１項該当）
学位論文の題目	Fundamental Study on Pyrolysis of Bromine Containing High Impact Polystyrene (HIPS-Br) in the Presence of Polyolefins （臭素含有耐衝撃性ポリスチレン（HIPS-Br）のポリオレフィン類共存下における熱分解に関する基礎研究）
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学位論文内容の要旨

The background of this study has come from the recycling issues of high impact polystyrene (HIPS-Br) as a typical plastics used for electronic products such as covering materials for TV-set, personal computer, refrigerator and washing machine etc. HIPS-Br is the mixture of polystyrene (about 77 wt%), polybutadiene (about 8 wt%), brominated flame retardant (BFR) (about 10 wt%) and synergist diantimony trioxide, Sb_2O_3 (about 5 wt%). Most of electronic appliances are protected by BFR for safety reason. The brominated flame retardants (BFRs) are decabromo diphenyl oxide (DDO), decabromo diphenyl ethane (DDE), tetrabromobisphenol-A (TBBP-A) or hexabromo cyclododecane (HBCD). DDO as the most common BFR has been used on the market since 1980`s. Due to the carbon linking with oxygen between aromatics rings of DDO, there is a possibility of formation of polybrominated dibenzo-p-dioxin which has strong toxicity. DDE has been an alternative for replacing the application of DDO.

Most researches on brominated flame retardant are focused on the modification of brominated flame retardant to extinguish flame during combustion. However, the study on the mechanism and fate of brominated flame retardant and synergist in reductive pyrolysis atmosphere is a new research field and very few. The thesis consists of two sessions; the fundamental study on pyrolysis of bromine containing HIPS-Br and the application of the fundamental study for decreasing the bromine content in liquid products without any catalyst or sorbent by applying the two-steps temperature pyrolysis.

In Chapter 1, the general view of plastics production, plastics recycling methods, and recent studies on pyrolitic recycling of the chlorine and bromine containing plastics are stated and finally the objectives of this thesis are stated.

Chapter 2 gives the fundamental experimental results and discussion on the pyrolysis of four types of HIPS-Br samples at 430 ^oC with two types of brominated flame retardants (DDO and DDE) and with and without Sb_2O_3. It has been found that degradation of HIPS-Br in the presence of Sb_2O_3 started at lower temperature than the HIPS-Br without Sb_2O_3. The presence of Sb_2O_3 increased the rate of degradation, and accelerated formation of liquid products. The role of Sb_2O_3 was effective suppressing the HBr in gaseous products and formation $SbBr_3$, and decreasing organic bromine compounds in liquid products. Interesting finding was that inorganic compound, $SbBr_3$ was always found in liquid product by dissolving into organic hydrocarbon liquid. Either DDO or DDE gave almost similar results on material balance of pyrolysis products;　bromine-free hydrocarbons and brominated compounds in liquid products, gaseous products and residues.

Furthermore, commingle effect of polystyrene (PS), polypropylene (PP) and polyethylene (PE) (each 20 wt%) in pyrolysis of HIPS-Br also has been studied for understanding the effect of each polymer in Chapters 2, 3 and 4. It has been found that HIPS-Br pyrolysed independently due to the degradation of HIPS-Br occurred at lower temperature. As results, these wide-use polymers (PS, PP and PE) had weak interaction with HIPS-Br during pyrolysis (Chapters 2, 3 and 4).

In Chapters 5 and 6, as the application of results from fundamental study in Chapters 2 to 4, the two-steps pyrolysis method has been applied for the model waste of electric and electronic equipment (WEEE). The model WEEE was composed of mixture of PS, PP and PE (90 wt%) and HIPS-Br (10 wt%). The main purpose was to decrease the bromine compounds in liquid products without any catalyst/sorbent. Two-steps pyrolysis has been done by keeping at the lower temperature (step-1 at 330 ^oC) and higher temperature (step-2 at 430 ^oC). The two-steps pyrolysis demonstrated that bromine compounds were effectively concentrated in small amount of step-1 liquids rather than the step-2 liquids. The two-steps pyrolysis showed to be a promising method to collect bromine resources such as brominated organics and inorganic $SbBr_3$ in step-1 liquid.

論文審査結果の要旨

近年、廃プラスチックの再資源化の観点からポリスチレン（PS）やポロプロピレン（PP）、ポリエチレン（PE）など汎用プラスチックの熱分解（還元雰囲気）技術の研究が進んできている。しかし、廃家電（WEEE）プラスチックに混入した臭素含有耐衝撃性ポリスチレン（HIPS-Br）のHIPS－Brの熱分解挙動は多くの点が不明であり、また、その他の汎用プラスチックとの熱分解時の相互作用に関する系統的な研究はほとんど見られない。本論文は難燃剤臭素化合物を含む耐衝撃性ポリスチレン（HIPS-Br）のポリオレフィン類共存下における熱分解に関する一連の基礎研究の内容をまとめたものである。研究の成果は、以下の３項目に要約できる。

１．代表的な難燃剤臭素化合物であるdecabromo diphenyl oxide (DDO)およびdecabromo diphenyl ethane (DDE)を含む耐衝撃性ポリスチレン（HIPS-Br）の熱分解の挙動を明らかにし、生成する気体、油、固体残渣および有機臭素化合物の生成機構を論じた。

２．臭素含有耐衝撃性ポリスチレン（HIPS-Br）のポリオレフィン類共存下おける熱分解機構を明らかにし、あわせて難燃助剤として汎用される酸化アンチモンの影響を実験および理論面から論じた。

３．油化プロセスを低温処理（330℃）および高温処理（430℃）に分けて行うことにより、燃料としてリサイクル使用する場合、有害な有機臭素化合物をほとんど含まない熱分解油を得ることに成功した。

以上、述べたごとく、上記の研究成果は学術的に優れており、工学的応用の可能性も高いものであるので、博士（学術）に値すると認める。