Recycling TV Cabinets Using Orange Oil

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A new technique of recycling TV cabinets containing a halogenated flame retardant has been developed. About 90% of the halogenated flame retardant, decabromodiphenyether (DBDPE), can be removed from the limonene (orange oil) used to dissolve TV cabinets using a centrifuge because the solubility of DBDPE is 0.2 wt% at 20℃in d-limonene. Residual DBDPE in the d-limonene solution can be removed at 60℃within a hour using 5 wt% of the adsorbent of an alkoxide. Residual DBDPE of the HI-PS is under 0.1wt%. We demonstrated that a TV cabinet with 10% flame retardant can be decomposed using sub and supercritical water containing hydrogen peroxide. 89% of the ionic bromine (Br^-) in the flame retardant was recovered after supercritical oxidation.

Introduction

High-impact styrene (HI-PS) is widely used for the cabinets of electrical products. Japanese regulations on recycling electrical products stipulate that TV cabinets with a flame retardant have to be recycled. Some HI-PS waste is recycled to make injection molding material, but recycled HI-PS does not retain its original mechanical properties due to contamination by other materials and thermal degradation. In this paper, we report on a new technique of recycling TV cabinets containing a halogenated flame retardant by using d-limonene, an orange oil and the decomposition of the flame retardant using supercritical water.

Materials and methods

The front cover of a TV cabinet contains about 10wt% of a halogenated flame retardant while the rear cover contains no flame retardant. The molecular structure of a TV cabinet is shown in Fig. 1. Decabromodiphenyether (DBDPE) is the flame retardant used in TV cabinets. d-limonene, which is extracted from orange peel, can dissolve about 30wt% of the front and rear cover with a rubber content of 4.5wt% at room temperature. The TV cabinet's molecular weigh is 170,000. 90wt% of the halogenated flame retardant and contaminants such as metal and plastic parts and plastic labels were separated out using a centrifuge. The limonene solution was heated to about 230 ℃ and separated into HI-PS and limonene under vacuum. The molecular weight

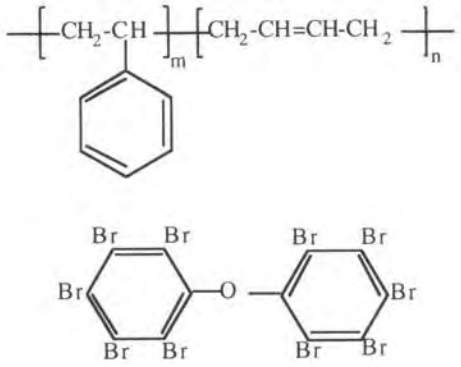

Table I
Temperature of water inside the reactor over time

Time (min)	Temperature (℃)
50	238
60	271
70	314
81	351
90	376
109	394
114	398

Fig.1 Molecular structure of HIPS and DBDPE

of recycled HIPS, residual limonene and the flame retardant content of HIPS were measured by GPC (gel permeation chromatography) using a refractive index meter. The mechanical properties of recycled HIPS were measured using a Tensilon (strain speed : 5 mm / min), and an impact strength meter in accordance with ASTM D638 and D256. Oxidation by sub and supercritical water was applied to the decomposition of the flame retardant. The volume of the reactor was 100ml with a sample weight of 180-200mg. Decomposition was done at at 400℃, 38MPa as a final condition using deionized water containing hydrogen peroxide with a flow rate of 20 ml / min. Table I shows the rise of water temperature inside the reactor over time.

Results and Discussion

Mechanical properties of the recycled material

The material recycled from the rear cover with no flame retardant has the same tensile strength, bending modulus, impact strength and heat resistivity of new material, as shown in Table II. We found that recycled HI-PS retains its original mechanical properties because almost no decomposition of polystyrene and rubber occurs, as measured by the loss of molecular weight and NMR analysis. d-limonene dissolves only HI-PS; the degree of dissolution of other plastic is less than 2 wt% [1].

Table II
Mechanical properties of recycled HIPS

Sample	Tensile strength (MPa)	Elongation (%)	Impact strength (Jm-1)	Softening temp (℃)	Molecular weight Mw
New HIPS	28	43	5.9	93	230000
Recycled	32	31	6.1	94	220000

Removing the flame retardant

We have developed a technique for removing the residual flame retardant from the limonene solution using basic adsorbents such as magnesium oxide derivatives and alkoixdes. After DBDPE in a 25 wt% TV cabinet solution was removed by a centrifuge, the limonene solution was treated at 60 ℃within a hour using 5 wt% of an adsorbent such as alkoxides. Residual DBDPE of the HI-PS is under 0.1wt%, which shows that 99 wt% of a flame retardant can be removed using an adsorbent.

Decomposition of a flame retardant

194 mg of the TV cabinet sample (2-3 mm grain) was decomposed using sub and supercritical water containing 1.25 wt% of hydrogen peroxide. Figure 2 shows the concentration of total organic compound and ionic bromine measured by a TOC meter and ion-exchange chromatography. Decomposition occurs at about 270℃, and the maximum concentration of TOC and ionic bromine peak were observed at 340℃ and 370℃. This difference might be caused by the difference in the chemical structure of HIPS and DBDPE. The ratio of ionic bromine to the total bromine in the decomposition products was 89%. We speculate that supercritical water oxidation will promote the decomposition of aromatic flame retardants because the maximum decomposition peak was observed in the vicinity of the supercritical point.

Conclusion

A new TV cabinet recycling technique, which uses orange oil, has been developed. The recycled HI-PS has the same mechanical properties as new HI-PS. 99% of DBDPE can be removed from the TV cabinet solution using a basic adsorbent of alkoxide. Using supercritical water oxidation is useful to decompose of a flame retardant. 89 % of ionic bromine (Br^-) can be recovered.

Acknowledgements

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References

1. Tsutomu Noguchi, Mayumi Miyashita and Haruo Watanabe, Nippon Kagaku Kaishi, **1999**, 615.

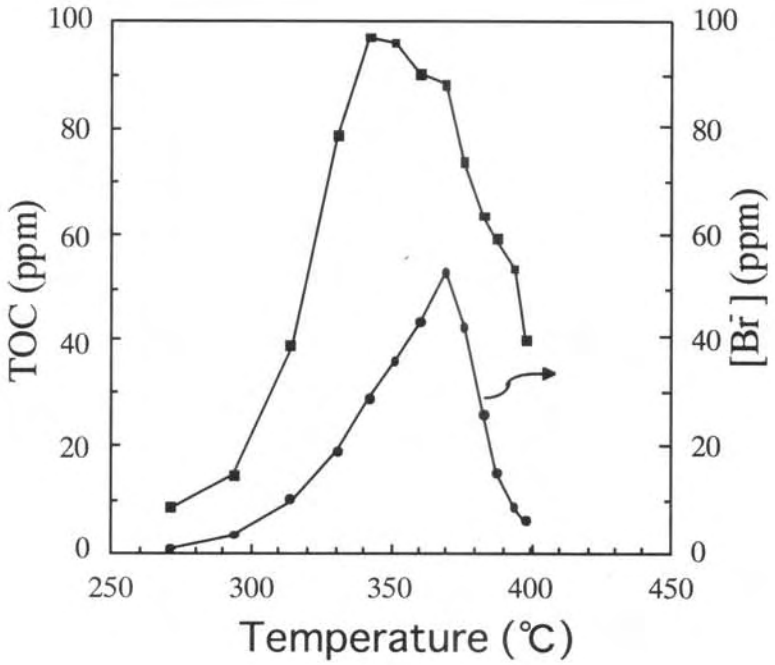

Fig.2 Concentration of total organic compound and ionic bromine.