

Recycling Process for the Resins Containing Brominated Flame Retardant

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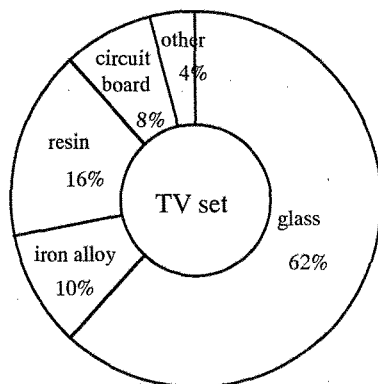
Resin is one of the most difficult materials to recycle from end-of-life products because of the use of diverse additives. Thermoplastic resins containing flame retardant have been widely used as burn-resistant materials such as cabinets for TV or personal computer. However, some brominated compounds used as flame retardant have been said to generate brominated-dioxins when incinerated at low temperature. Thus, recycling of resins containing flame retardant is a key step in increasing the recycling ratio.

We have developed a recycling process for safely separating flame retardant from used resins. This technology employs a continuous extraction process using a kneading extractor, contacting with a solvent that dissolves only flame retardant. Of course, the solvent can be repeatedly used. This extraction process is performed at relatively low temperature (<200°C), and therefore it does not damage the physical characteristics of the resin. This means that it is possible to use recycled resin rather than virgin one for some parts of new products.

Key words: flame retardant, thermoplastic resin, material recycling process, kneading extractor, brominated-dioxin

1. INTRODUCTION

Thermoplastic resins with flame-retardant are used to enhance the safety of many home appliances. Figure 1 shows the composition ratio of television set materials. The most component of resin, which occupy 16% of all, is flame-retardant agent used as cabinets. The resin parts are relatively easy to dismantle.



manufactured in 1996
(based on a survey conducted by the
Association for Electric Home Appliance)

Fig.1 Component ratio of TV sets

On the other hand, the deadline for halting the use of brominated flame-retardant agents is approaching. For example, the European Directive on Waste Electrical and Electronic Equipment (WEEE) dictates that a certain proportion of plastics containing flame-retardant agents be collected, and the Directive on Restrictions of Hazardous Substances (RoHS) prohibits the use of specific brominated flame-retardant agents, such as polybrominated biphenyl (PBB) and polybromodiphenyl ether (PBDE). Matsushita Electric Group is now

grappling with the task of stopping the use of such specific brominated flame-retardant agents before 2005, which is called the Green Plan 2010 project.

We have already developed the Pla-selector, a plastic type/flame-retardant agent kind identifying unit¹. We have more recently developed a flame-retardant agent/plastic separating technology for post-processing the plastics identified using the Pla-selector. An outline is given below.

2. RECYCLING TECHNOLOGY FOR FLAME-RETARDANT RESINS

The recycling methods of flame-retardant plastics have up to now been studied mainly by photocopy machine manufacturers. In most cases, the plastic parts are collected, broken up, mixed with virgin material, and re-used. This method, however, does not enable the use of different plastics containing different types of flame-retardant agents, or it is restricted to plastics containing only non-brominated flame-retardant agents. Plastics manufacturers are proposing the thermal recycling of plastics containing flame-retardant agents and are examining its practical use including the separation out and removal of halogen gases².

We have now developed a material recycling method that extracts flame-retardants from resins to provide environmentally safe products through the improvement of the recycling ratio of collected televisions, reduction of waste, and the active use of recycled resin.

3. EXTRACTION AND ELIMINATION OF FLAME-RETARDANT AGENTS

3.1 Principle

Separating out and removing a non-soluble flame-retardant agent such as decabromodiphenyl ether (DBDE) for recycling is usually done by first separating the soluble components such as resins from the non-soluble components such as DBDE using solvents for the resins, then separating the resin from the solvent³.

However, in the case of the flame-retardant agents discussed here, the retardants readily dissolve in the solvent for resin, meaning that another process is necessary, such as mixing the solution with a second solvent, such as alcohol, to precipitate out the resin and allow it to be removed (Fig.2 A). We have found that flame-retardant agents can be separated from resin by using a solvent in which only the flame-retardant agent is soluble (Fig.2 B).

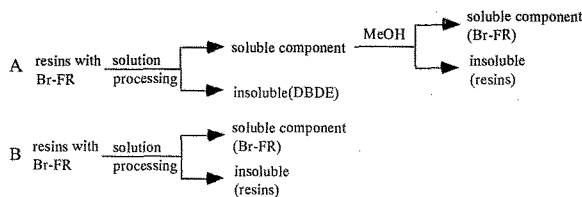


Fig.2 Separation process for resin and flame retardant

3.2 Method of extraction

To realize the extraction of the above-mentioned flame-retardant agents, we have tried several methods, such as processing the resin by stirring it in heated solvent, or first grinding the resin into fine particles to speed the removal of the retardants. Our results showed that the separation process of resin and solvent after the treatment and the removal process of residual solvent in the resin need to be simplified to reduce total recycling costs. To solve this problem, we have developed a continuous-type kneading extraction unit. The schematic diagram and full view are shown in Fig. 3 and Fig. 4, respectively.

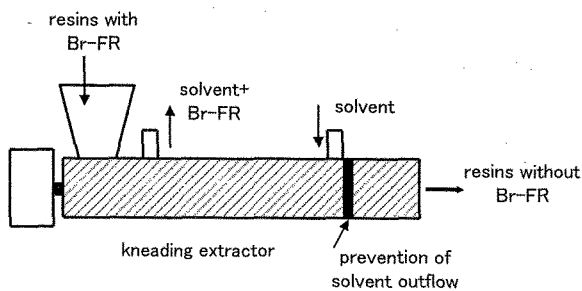


Fig.3 continuous-type kneading extraction unit

Thermoplastic resin containing flame-retardant are supplied by a hopper, and the solvent for flame-retardant agent extraction are supplied by the solvent inlet port, respectively, and then they are heated and mixed by a rotating screw in the kneading extraction unit. The solvent, from which the flame-retardant agent is extracted by providing a separating mechanism for the solvent component, is then drained through the solvent outlet port, and the plastic from which the flame-retardant agent is removed is ejected from the dice in the same way as a conventional molded piece.

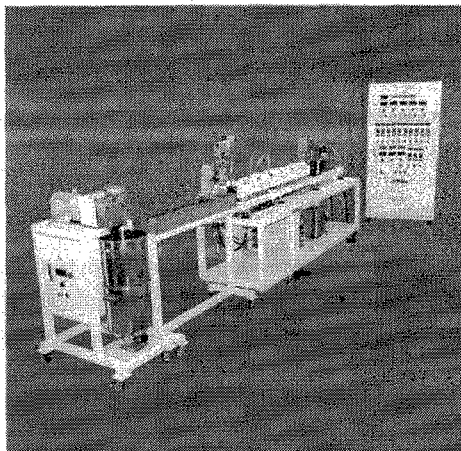


Fig.4 Full view of continuous-type kneading extraction unit

The recycled resin is prepared by removing the back covers from television sets collected at a recycling station, selecting the plastic using a Pla-selector, and crushing it about 5 mm in size. The resin is high-impact polystyrene, and the flame-retardant agent is a soluble brominated flame-retardant agent. To extract the flame retardant, the temperature of the extraction unit is set to 180 °C and a glycol-series solvent with a boiling point higher than 200 °C is used. In addition, to reduce the ratio of residual solvent in the resin, a ventilation study is carried out near the dice of the kneading extraction unit.

3.3 Device performance evaluation

Figure 5 shows the measurement results by GPC (Gel Permeation Chromatograph) before and after the treatment of the flame-retardant resin in the kneading extraction unit. For the solvent used in this unit, it is confirmed that only flame-retardant agent is removed from the resin components and no changes in molecular weight are observed in the polymer components of the resin.

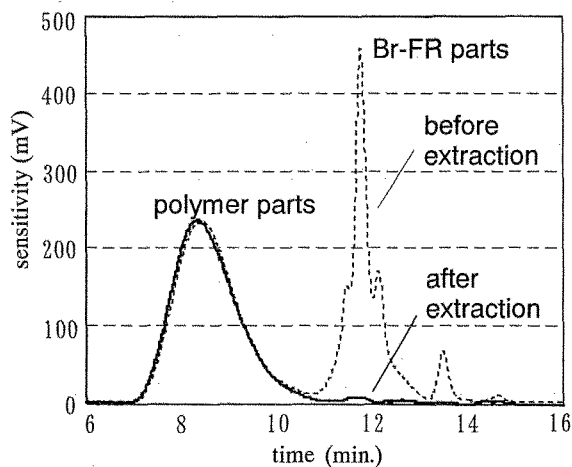


Fig.5 GPC chart of the kneading extracted polymer compared with collected polymer.

The flame retardant density in the resin can be reduced to 1% or less of its initial value by optimizing the screw structure such that the solvent and resin flow in opposite directions to each other, as shown in Fig.3, although the performance depends on the speed of revolution of the kneading extraction unit, the quantity of resin loaded, and the solvent-resin ratio. An analysis of flame retardant density is mainly conducted by GPC measurement, as shown in Fig. 5, and ion-chromatographic analysis is also conducted. In addition, it has been confirmed that the residual ratio of the solvent in the resin was reduced to 1% or less by the venting treatment. Analysis is also conducted of Br-Dx generation in the resin after extraction and Br-Dx generation in the resin when thermally treated at 600 °C; both results are under the detection limit.

In addition, antimony trioxide, which is added as an auxiliary flame-retarding agent to flame-retardant plastics, is also extracted using a solvent with a boiling point of about 200 °C. It is confirmed by ICP light emission analysis that the treatment reduced the initial composition of antimony by 90%.

3.4 Evaluation result of treated resin properties

For the resin obtained by the above-mentioned kneading extraction treatment, specimens are made and an Izod impact test and tension test are conducted according to JIS K7110 and JIS K7113, respectively. The tests are also conducted in the case when virgin plastic, raw material of collected resin, and collected resin were crushed and only melting/kneading was conducted for comparison. The results are shown in Table I.

Table I Properties of the kneading extracted resins

	virgin resin	collected resin	treated resin
Tensile yield strength (kgf/cm ²)	202	211	273
Tensile fracture strength (kgf/cm ²)	160	159	244
Yield elongation (%)	19	26	29
Izod impact strength (kJ/m ²)	6.0	4.6	9.5

Collected resin shows less impact strength than virgin material, but tensile strength was not markedly different. On the other hand, both Izod impact strength and tensile strength of the collected resin increased significantly when the flame-retardant agent had been extracted (treated resin), probably because the flame-retardant agent has a plasticizing effect, which disappears when the flame-retardant agent is removed. Dupont impact strength is also evaluated and revealed to have less difference than that of virgin material.

It is concluded from these results that the strength does not decrease, as might be expected for collected plastic, but instead increases due to the removal of flame-retardant agent.

4. COLLECTION AND REUSE OF EXTRACTION SOLVENT

It is essential to recycle and re-use the solvent used in the kneading unit after separating out the flame-retardant agent. Although solvent loss may occur during the extraction process of resins containing flame-retardant and the collection process of the solvent, the processing cost per unit of resin can be reduced by reducing the solvent quantity extracted with flame-retardant agent as final residue. After examining reduced-pressure distillation of the solvent used for flame-retardant agent extraction using various solvent collection devices, the distillate and residue are collected separately. The collected residue is found to have a high ratio of solid content and the residual solvent density in the residue is sufficiently reduced.

On the other hand, the results of GC analysis showed the collected solvent to have a peak identical to that of virgin solvent, with no generation observed of deteriorated components or impurities. This indicates that the solvent can be repeatedly used.

5. SUMMARY

As described above, it has been found that the flame-retardant agent in the resins from collected television cabinets can be removed by a continuous-type kneading extraction unit, allowing the resins to be effectively recycled. In addition, auxiliary flame-retardant agents can also be removed by using more than one solvent.

While there are many studies for recycling methods of flame-retardant resins, our newly developed technology can secure undamaged resin with satisfactory properties. In addition, processing costs are low because the solvent can be used repeatedly after the separation treatment by distillation to remove the flame-retardant agents.

In the future, we will examine the potential for practical application of this technique by scaling up the kneading extraction unit and solvent collection unit.

6. REFERENCES

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