Behavior of Bromine in Thermal Decomposition of Paper Base Phenolic Laminate Wastes

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We investigated thermal properties and a behavior of bromine in thermal decomposition of paper base phenolic resin laminate wastes containing polybrominated flame-retardants. The thermal properties of the phenolic laminate wastes were measured by thermogravimeter and conduction-type scanning calorimeter (TG-CSC). The weight losses of the wastes by thermal decomposition were mainly classified as three sections in the range from 40°C to 600°C. The enthalpy (ΔH) of the thermal decomposition was determined to be 103.98 cal/g. The material balance of decomposition components was measured by batch-type thermal decomposition equipment. Contents of carbon residue, liquid and gas decomposed at 800°C in vacuum were approximately 37wt%, 48wt% and 15wt%, respectively. Bromine contents of the carbon residue and the liquid were less than 0.02wt% and 10wt%, respectively. These results are important values in application as carbon materials and in carbonization process of these wastes.

Introduction

Phenolic resins have been currently applied to moldings of electrical appliances and vehicles parts, laminates, shell-molds and insulators because of excellent electrical, heat-resistant and mechanical properties. As the cured phenolic resins can neither be melt nor be dissolved in any solvents, it is difficult to recycle. Most of the phenolic resin wastes were still discarded to a reclaimed land or were destroyed by fire. Recently, we have been developing a novel recycling method of paper base phenolic resin laminate wastes (non flame-retardants) by carbonization, in which a slip casting and an extrusion molding of carbon precursor powders, an application of carbon precursor powders to activated carbons [1, 2] and an epoxy resinification of decomposition liquid [3, 4] were contained. In application, these activated carbons which are more excellent than usual activated carbons are used as electrode materials for an electric double layer capacitor. Most of paper base phenolic resin laminates, however, employed for printed circuit boards have been contained flame-retardants under the product standard for fire safety.

In this study, thermal properties and a behavior of bromine in thermal decomposition of phenolic laminate wastes containing polybrominated flame-retardants were investigated. The thermal properties were measured by means of an apparatus composed of thermogravimeter and conduction-type scanning calorimeter (TG-CSC). Material balance of decomposition components was also measured by a batch-type thermal decomposition equipment. And bromine analysis was carried out for decomposition components.

Materials and Methods

Materials. Wastes of paper base phenolic resin laminate used were laminate edges (resol type, 60 wt% of paper content), called as phenolic laminate wastes. They were contained tetrabromo bisphenol-A diglycidyl ether and tetrabromo bisphenol-A and were supplied by the laminates manufacturing company. These laminates were conventional products employing for housing parts of lighting appliances.

TG-CSC measurement. The themogravimetric properties, specific heat capacities at constant pressure (C_p) and the enthalpy value (ΔH) of the phenolic laminate wastes were measured by TG-CSC (DTC-7000, Shinku-Riko, Inc.). TG-CSC [5] is able to run quantitative measurements exactly in case of thermal decomposition-vaporization and its following weight changes of the sample. The calorimetric measurements with TG-CSC were carried out using a alpha-alumina as a standard material.

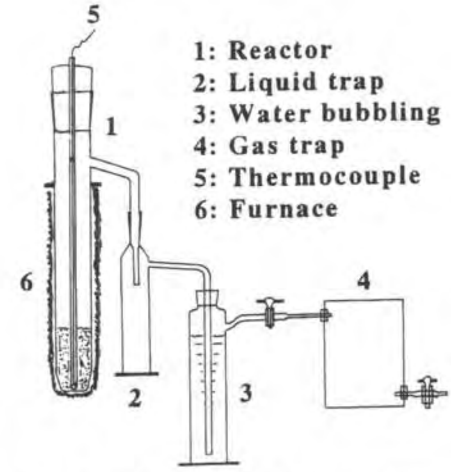

Fig. 1 Batch-type thermal decomposition equipment.

Analysis of Thermal Decomposition Components. The batch-type thermal decomposition equipment is shown in Fig. 1. It consisted of major components numbered from "1" to "6". In this equipment, the phenolic laminate wastes were decomposed at 600°C, 700°C and 800°C in vacuum and the material balance of decomposition components (carbon residue, liquid and gas) was measured. The carbon residue and liquid were obtained in a batch reactor "1" and in an air-cooled trap "2", respectively. The gas after bubbling in distilled water "3" was collected in a gas trap "4". Bromine contents of the carbon residue and liquid were analyzed by combustion method. Gas analysis was carried out by means of gas chromatography. Moreover, anion analysis of water solution bubbled by decomposition gas was performed by ion chromatography.

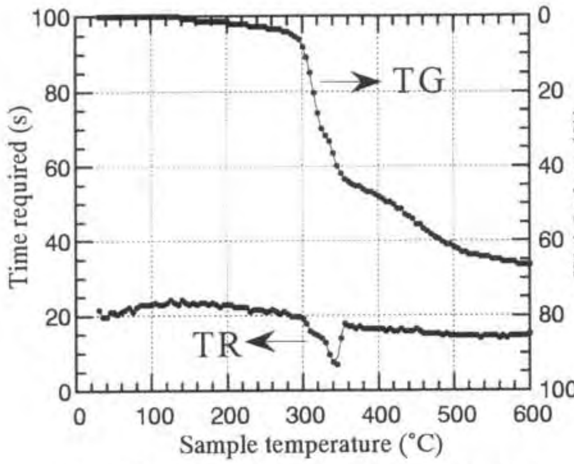

Fig. 2 TG-CSC curve of paper base phenolic resin laminate wastes.

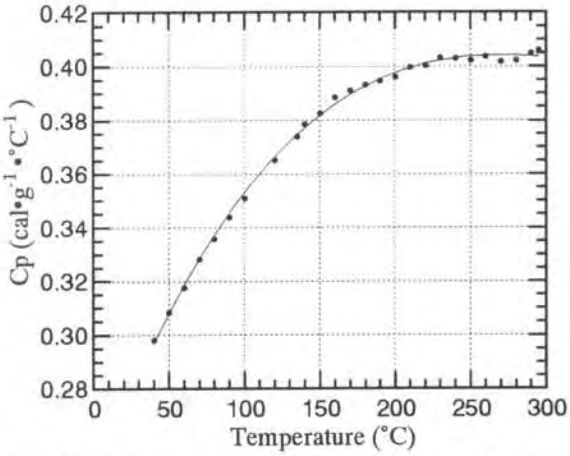

Fig. 3 Cp data of paper base phenolic resin laminate wastes. Temperature range: 40-295°C.

Results and Discussions

Thermal Behavior of Phenolic laminate wastes. Fig. 2 shows the TG-CSC curve of the phenolic laminate wastes in the range from 40°C to 600°C. It was found that weight losses by thermal decomposition were mainly classified as three sections. First, the weight loss began from approximately 130°C due to vaporization of moisture on the wastes. Secondly, a precipitous weight loss occurred in the range from near 300°C to 350°C. In this range, the paper base phenolic resin was decomposed to the mono-phenol derivatives [4] because of fission of C-C bonds linked a phenol unit with a methylene group ($-CH_2-$). Finally, the gradual weight loss continued over approximately 350°C, resulting in the carbonization of paper based phenolic resin.

Thermal Properties of Phenolic laminate wastes. The TR curve in Fig. 2 shows a trough in the range from near 300°C to 350°C, and the trough temperature was approximately 345°C because of exothermic behavior by condensation reaction of the residual methylol groups ($-CH_2OH$). Fig. 3 shows the specific heat capacity at constant pressure (C_p) of the phenolic laminate wastes in the range from 40°C to 295°C calculated by the TR curve. The C_ps of the wastes were determined to be from 0.298 cal/g°C to 0.406 cal/g°C. The enthalpy (ΔH) of the wastes in the range from 40°C to 355°C, in which the thermal decomposition mainly occurred, was determined to be 103.98 cal/g. Since these results, which have been hardly measured so far, these will be useful in making a thermal processing plant and equipment.

Material Balance of Thermal Decomposition Components. The material balance of thermal decomposition components of the phenolic laminate wastes are shown in Table 1. It was found that the content of the carbon residue decreased and the content of the gas and liquid increased with increasing decomposition temperature. The yield of the carbon residues that were applicable to high-performance carbon materials was from 37wt% to 40wt%.

Table 1 Material balance of thermal decomposition components of paper base phenolic laminate wastes.

Decomposition temperature (°C)	Carbon residue (wt%)	Liquid (wt%)	Gas a) (wt%)
600	40.4	46.5	13.1
700	38.0	47.5	14.5
800	36.8	48.3	14.9
800 b)	37.3	47.8	14.9

a) Calculated. b) Without water bubbling.

Table 2 Bromine contents of the thermal decomposition liquid and the carbon residue.

Sample (decomposition temperature)	Bromine content (wt%)
Liquid (800°C)	10.00
Carbon residue (600°C)	0.02
Carbon residue (700°C)	≤0.02
Carbon residue (800°C)	≤0.02

Analysis of Thermal Decomposition Components. Bromine contents of the thermal decomposition liquid and the carbon residue are shown in Table 2. Bromine contents of the liquid and the carbon residue decomposed at 800°C were less than 10wt% and 0.02wt%, respectively. These results are important values in application as carbon materials and in carbonization process of these wastes. Table 3 shows the decomposition gas component analyzed. It can be seen that various hydrocarbons ($C_3 - C_5$) and CO_2 were contained in the gas. Furthermore, it is due to evolve lower hydrocarbons ($C_1 - C_2$), H_2 and HBr in these thermal decomposition processes. The gas decomposed at 800°C and unbubbled through distilled water contained higher content of CO_2. Table 4 shows the anion of water solution bubbled by thermal decomposition gas. It was considered that the Br^- ion was derived from flame-retardants, and the Cl^- ion and SO_4^{2-} ion were derived from bleaching agents and filler for paper. The Br^- ion and SO_4^{2-} ion decreased with increasing decomposition temperature.

Table 3 Analysis of the thermal decomposition gas.

Decomposition temperature (°C)	Gas content (vol%)					
	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5H_{12}	CO_2
600	0.71	0.77	0.37	0.38	0.14	0.09
700	0.59	0.61	0.27	0.27	0.10	0.00
800	0.54	0.56	0.30	0.23	0.10	0.16
800 a)	0.72	0.80	0.23	0.41	0.00	14.56

a) Without water bubbling.

Table 4 Anion analysis of water solution bubbled by the thermal decomposition gas.

Decomposition temperature (°C)	Br^- (wt%)	Cl^- (wt%)	SO_4^{2-} (wt%)
600	0.037	0.002	0.022
700	0.034	0.003	0.020
800	0.018	0.002	0.017

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