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Measurement of the Specific Heat of Plastic Waste/Fly Ash Composite Material Using Differential Scanning Calorimetry

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Abstract Plastic waste/fly ash composite, which is made mostly from plastic waste and fly ash, is one of the materials developed for the purpose of recycling. Currently, the composite is used for cable troughs shielding underground lines. However, there exists little information concerning the thermophysical properties of the composite. Thermophysical properties and the structure of the composite must be determined to estimate the heat transfer in the composite and create the different proportions of the composite material. This article deals with measurements of the specific heat of the plastic waste/fly ash composite and its components using a differential scanning calorimeter. The composite sample, which ranged from 10 mg to 19 mg in mass, was cut from a cable trough. The standard reference material is synthetic sapphire disks of 19.6 mg and 29.6 mg in mass. The specific heat of the plastic waste/fly ash composite increases from 1.25 $kJ \cdot kg^{-1} \cdot K^{-1}$ to 1.59 $kJ \cdot kg^{-1} \cdot K^{-1}$ at temperatures from 305 K to 360 K. The uncertainty for the specific heat data of the composite is estimated to be about 4 %. In addition, the specific heat value depends heavily on the content of the plastic waste.

Keywords Composite material · DSC · Fly ash · Plastic waste · Recycle · Specific heat

1 Introduction

Plastic waste/fly ash (which the authors call "PWFA" for short) composite, which is made mostly from plastic waste and fly ash, is one of the materials developed for the

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purpose of recycling. Irregular plastics in shape and size, different types of plastic, and plastics unsuitable for recycling with an existing technology can be mixed with the ingredients of the composite. The composite can be recycled repeatedly. Currently, the PWFA composite is used for cable troughs shielding underground lines. The thermal conductivity and specific heat of the PWFA composite must be determined to estimate the heat transmitted through the cable trough and the temperature rise in the cable and cable trough, because an excessive temperature rise of the cable causes serious problems. However, there exists little information concerning the thermophysical properties of the PWFA composite. In addition, it is not easy to estimate the thermophysical properties of the PWFA composite by using conventional theoretical models for the dispersed composite material [1], because the thermophysical properties of fly ash and of the blended plastic formed of different plastics are not known.

The goal of this work is to obtain the fundamental data on the thermal conductivity, specific heat, and structure of the PWFA composite to determine the heat transfer in the composite and estimate the thermophysical properties of different proportions of the composite material. The authors previously measured the thermal conductivity of the PWFA composite using the guarded hot plate apparatus and observed the cutting surface of the PWFA composite using a metalloscope [2]. The thermal conductivity was about $0.4\,\mathrm{W}\cdot\mathrm{m}^{-1}\cdot\mathrm{K}^{-1}$ at 300 K. In addition, it was found that fly ash disperses at irregular intervals in the continuous phase composed mainly of plastic wastes.

This article deals with the measurements of the specific heat of the PWFA composite and its components using a differential scanning calorimetry (DSC). The specific heat measurements are repeatedly carried out at temperatures not exceeding 365 K to prevent the melting of the plastic components. The specific heat data of the PWFA composite, fly ash, and the blended plastic composed of the polyethylene and polypropylene resins, the estimation of the specific heat of the fire retardant, and the uncertainty of the specific heat of the PWFA composite are described.

2 Features of the PWFA Composite Sample

Specimens of the PWFA composite were cut from a cable trough. The cable trough is the first recycled product made from recovered plastic waste materials. Data on the composition of the PWFA composite are listed in Table 1. The plastic waste and fly ash components account for over 80 % of the total mass. The recovered plastic waste mainly consists of polypropylene and polyethylene resins used for home wrapping materials. Fly ash was generated at a domestic coal-fired power plant. Besides a small amount of glass fiber as reinforcement, a fire retardant is added to the PWFA composite. On the other hand, the name, chemical formula, composition, and some details concerning the fire retardant are not disclosed by the manufacturer of the PWFA composite, because it is a industrial proprietary information.

Figure 1 shows observations of the particles of fly ash using a scanning electron microscope (SEM) and the polished surface of the PWFA composite using a metalloscope [2]. Fly ash particles were globular in shape and under 60 μm in diameter. The round particles of fly ash disperse at irregular intervals in the matrix, as shown in Fig. 1b. Each particle of fly ash is surrounded by the matrix. In contrast, the form of the matrix is a continuous phase. Although fly ash was heated to the melting

Table 1 Composition of PWFA composite

Components		Contents per unit mass (%)
Plastic waste		
Polypropylene	62	45
Polyethylene	36	
Other	2	
	Sum: 100 %	
Fly ash		38
Glass fiber		2
Fire retardant		15
		Total: 100 %

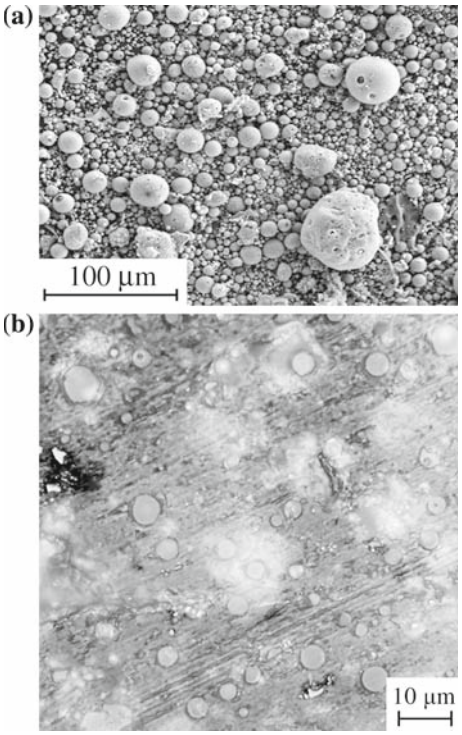

Fig. 1 Observations of (**a**) particles of fly ash and (**b**) polished surface of PWFA composite

temperature of the plastic waste and mixed with the plastic waste, the broken and deformed particles of fly ash could not be found. It is quite certain that the matrix is composed of the plastic waste and fire retardant, but the distribution of plastic and fire retardant components and some details concerning the matrix are unclear.

To measure the specific heat of the PWFA composite, the authors prepared granular and plate samples of the composite. The granular sample, which was grated, had a grain size of not more than about 0.5 mm. In the case of plate samples, the sample surfaces were polished with sandpaper which has an abrasive particle size of 9 μm. In addition, the surface was buffed with a polishing solution containing aluminum particles 0.1 μm in size. After the polished sample was cleansed with ion-exchange

water inside an ultrasound bath, it was dried in a thermostatic chamber set at a constant temperature of 323 K. The plate sample had a size of about $2.5 \times 2.5\,\mathrm{mm}^2$ and a thickness of about 1 mm or less. The composite samples ranged from about 10 mg to 19 mg in mass.

3 Measurement Method

The specific heat was measured using a heat-flux differential scanning calorimeter [3]. The measurement sensitivity of the differential heat of the calorimeter is within 1.6 μW at temperatures from −150 °C to 725 °C. Specimens, the standard reference material, and sample (test substance) were placed into a separate aluminum capsule of 15 μL in capacity. The aluminum capsules ranged from 206.8 mg to 206.9 mg in mass. The capsule was sealed with a sealer.

The standard reference materials consisted of synthetic sapphire disks of 19.6 mg and 29.6 mg in mass. The data used for the specific heat of synthetic sapphire [4] are shown in Table 2. The masses of the specimen and capsule were measured using an electronic balance with a sensitivity of 0.01 mg. The uncertainty for the mass measurements was estimated to be within ±1 %.

To determine the specific heat of the sample, it is necessary to obtain the DSC curves of the empty capsule and capsules containing the specimen using the DSC. The DSC curves were obtained according to the following steps [3,5]. Figure 2 shows a schematic diagram of the heat-detecting element of the calorimeter [3].

Step 1: Four clean empty capsules were prepared. One of them received one sapphire disk as a standard reference material. Another capsule received the sample. The remaining capsules were empty. All capsules were sealed.

Step 2: The heating rate and the temperature range were inputted into a controller, i.e., the control program of temperature or the heating curve was fixed.

Step 3: An empty capsule was placed on the R-side capsule holder, as shown in Fig. 2. In addition, another empty capsule was placed on the other capsule holder (S-side capsule holder). The relationship between the DSC signal of the empty capsule and the temperature, i.e., the DSC curve of the empty capsule, was measured with the calorimeter.

Step 4: The empty capsule on the S-side capsule holder was replaced with the capsule containing the standard reference material (which is called the "reference material capsule" for short). As in the case of the empty capsule, the DSC curve of the reference material capsule was measured.

Step 5: The reference material capsule was replaced with the capsule containing the sample (which is called the "sample capsule" for short). As in the case of the empty capsule, the DSC curve of the sample capsule was measured.

During the series of measurements, the authors never touched the empty capsule on the R-side capsule holder and never removed the empty capsule. After the end of the measurements, the capsules remained in the apparatus and then were cooled by natural cooling. The capsules were not removed until the temperature of the capsule cooled to nearly ambient temperature. By following measuring steps 3, 4, and 5, three DSC curves were obtained.

Table 2 Specific heat data of metal oxides

Synthetic sapphire (Al_2O_3) [4]		SiO_2 [4]		Fe_2O_3 [4]		CaO [1]		MgO [1]	
T(K)	c (kJ · kg^{-1} · K^{-1})	T (K)	c (kJ · kg^{-1} · K^{-1})	T (K)	c (kJ · kg^{-1} · K^{-1})	T(K)	c (kJ · kg^{-1} · K^{-1})	T(K)	c (kJ · kg^{-1} · K^{-1})
290	0.757	316.65	0.784	292.35	0.642	300	0.753	300	0.924
300	0.779	334.05	0.806	301.23	0.654	340	0.777[a]	340	0.965[a]
310	0.800	348.85	0.821	310.20	0.667	380	0.801[a]	380	1.006[a]
320	0.819	367.55	0.842	319.04	0.677	400	0.813[a]	400	1.027[a]
330	0.838	381.25	0.861	327.77	0.687	500	0.873	500	1.13
340	0.856	390.65	0.876	336.53	0.697				
350	0.872	403.35	0.891	345.42	0.706				
360	0.889								
370	0.904								
380	0.918								
390	0.931								
400	0.944								

[a] Values calculated by the method of linear interpolation between the specific heat values at 300 K and 500 K

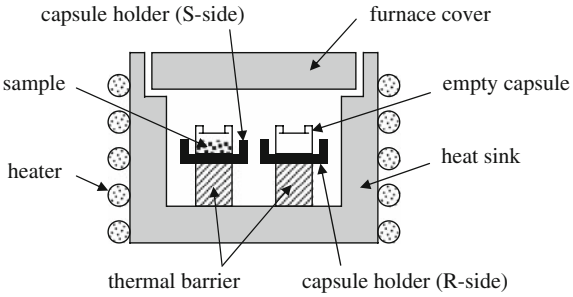

Fig. 2 Schematic diagram of heat-detecting element of calorimeter [3]

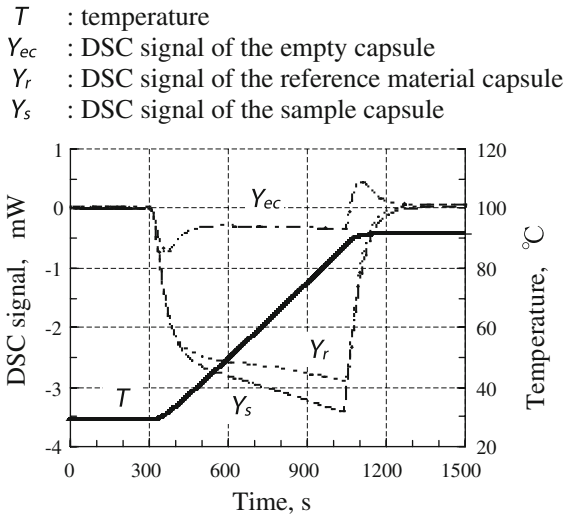

Fig. 3 Experimental results of DSC curves of PWFA composite

In this study, the specific heat measurements were repeatedly carried out at temperatures not exceeding 365 K to prevent the melting of the plastic components. The constant heating rates were set at $2\,\mathrm{K}\cdot\mathrm{min}^{-1}$, $5\,\mathrm{K}\cdot\mathrm{min}^{-1}$, and $10\,\mathrm{K}\cdot\mathrm{min}^{-1}$.

Figure 3 shows the experimental results of the DSC curves of the PWFA composite when the heating rate was set at $5\,\mathrm{K}\cdot\mathrm{min}^{-1}$. T is the temperature. Y_{ec}, Y_{r}, and Y_{s} represent the DSC signals of the empty, reference material, and sample capsules, respectively. The DSC signals showed transient behavior at the beginning and end of the rise of temperature. Furthermore, the DSC signal varied linearly with time or temperature, except during the two periods of transient behavior. The DSC data in the linear region were used for calculation of the specific heat. The specific heat of the sample c_{s} is given by

$$c_{\mathrm{s}} = \frac{M_{\mathrm{r}}}{M_{\mathrm{s}}} \times \frac{(Y_{\mathrm{s}} - Y_{\mathrm{ec}})}{(Y_{\mathrm{r}} - Y_{\mathrm{ec}})} \times c_{\mathrm{r}} \tag{1}$$

where c_{r} is the specific heat of the standard reference material, and M_{r} and M_{s} are the masses of the standard reference material and sample, respectively.

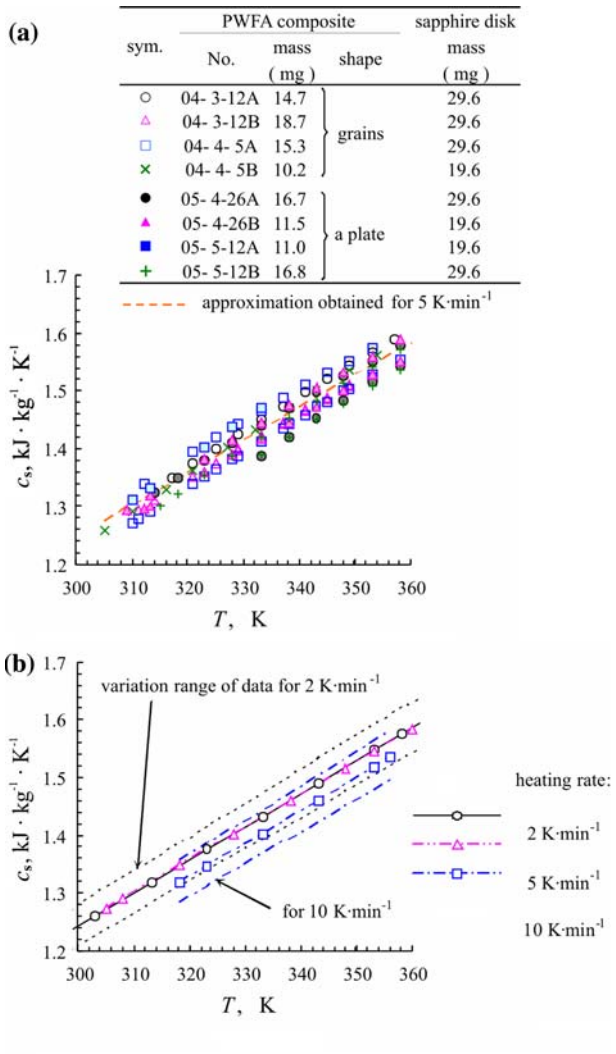

Fig. 4 Experimental results for PWFA composite: (**a**) heating rate of 5 K · min^{-1} and (**b**) effect of heating rate

4 Results and Discussion

Figure 4a shows the experimental results of the specific heat of the PWFA composite when the heating rate was set at 5 K · min^{-1}. The broken line on the figure represents the approximation obtained from the measured data by the least-squares method. The specific heat increased from 1.25 kJ · kg^{-1} · K^{-1} to 1.59 kJ · kg^{-1} · K^{-1} with an increase in temperature from 305 K to 360 K. In addition, the variation in the data was within ±3 %. Accordingly, the effect of the mass and shape of the composite sample on the measured data were within ±3 %.

Figure 4b shows the experimental results for the heating rates of $2\,K \cdot min^{-1}$, $5\,K \cdot min^{-1}$, and $10\,K \cdot min^{-1}$. In the case of the data obtained for the heating rates of $2\,K \cdot min^{-1}$ and $10\,K \cdot min^{-1}$, the variation range in the measured value is indicated in the figure. The data for $2\,K \cdot min^{-1}$ agreed with those for $5\,K \cdot min^{-1}$ within 0.2 %. However, the data for $10\,K \cdot min^{-1}$ were about 2 % lower than those for $5\,K \cdot min^{-1}$. In the case of heating rates of $2\,K \cdot min^{-1}$ and $10\,K \cdot min^{-1}$, the effect of the mass and shape of the composite sample on the measured data was within ±3 %. The authors speculated that recommended heating rates for reliable measurements of the specific heat of the PWFA composite are $2\,K \cdot min^{-1}$ and $5\,K \cdot min^{-1}$.

Taking into account the uncertainty for the measurement of mass and the variation and reproducibility of the present data, the uncertainty for the specific heat data was estimated to be about 4 % [6]. Additionally, based on the data obtained for $2\,K \cdot min^{-1}$ and $5\,K \cdot min^{-1}$, the specific heat of the PWFA composite can be expressed using the following equation, at temperatures from 305 K to 360 K:

$$c_s = -0.47 + 0.0057T \tag{2}$$

Figure 5 shows the experimental results for the specific heat of the fly ash particles when the heating rate was set at $5\,K \cdot min^{-1}$. Specific heat data of SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO, which are the constituents of fly ash [7], are plotted as shown in the figure. The specific heat data of these metal oxides [1,4] are listed in Table 2.

The specific heat increased from $0.7\,kJ \cdot kg^{-1} \cdot K^{-1}$ to $0.9\,kJ \cdot kg^{-1} \cdot K^{-1}$ with an increase in temperature from 310 K to 385 K. Additionally, the variation in the data was within ±7 %. Although the components ratio of the fly ash used for this study is

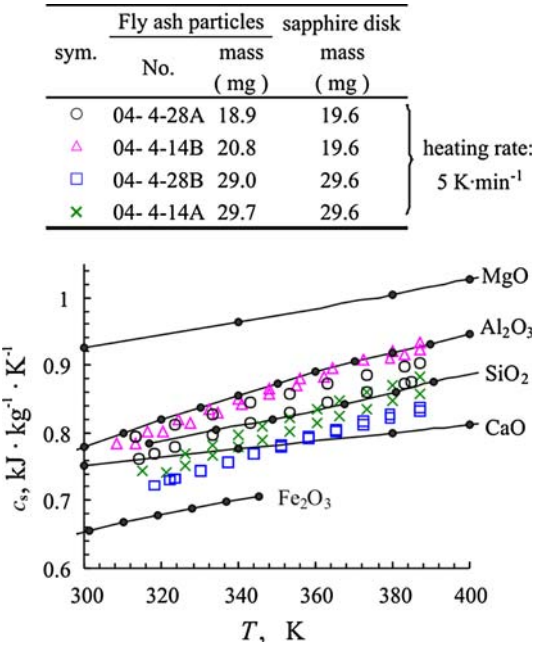

Fig. 5 Experimental results for fly ash particles

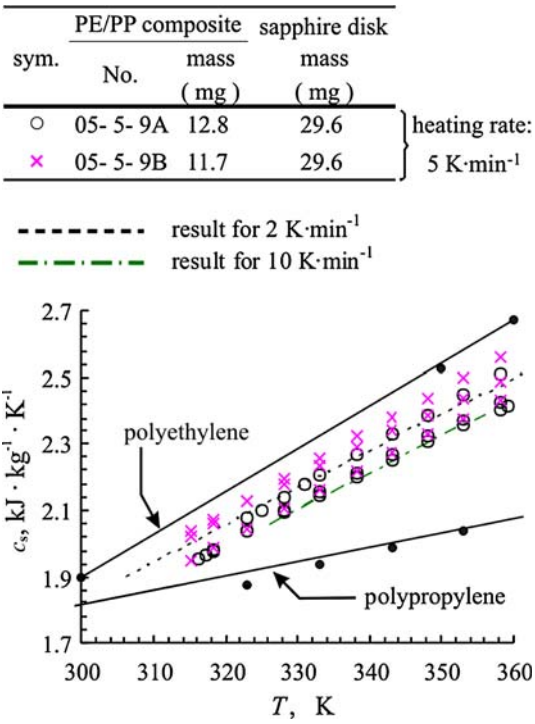

Fig. 6 Experimental results for PE/PP composite

Table 3 Specific heat data of polymers

Polyethylene[a] [1]		Polypropylene [8,9]	
T (K)	c (kJ · kg^{-1} · K^{-1})	T (K)	c (kJ · kg^{-1} · K^{-1})
300	1.90	273	1.7
350	2.53	323.2	1.88
360	2.67	333.2	1.94
		343.2	1.99
		353.2	2.04
		363.2	2.09
		400	2.1

[a] High-density polyethylene

unclear, SiO_2 and Al_2O_3 contents account for 70 % to 80 % of the total constituents of fly ash [7]. The specific heat of the fly ash used for this study is as large as those for SiO_2, Al_2O_3, and CaO.

Figure 6 shows the experimental results for the PE/PP (polyethylene/polypropylene) composite. The results for 2 K · min^{-1} and 10 K · min^{-1}, which are respectively indicated by a short dashed line and a dotted and dashed line, are approximated from the measured data by the least-squares method. Specific heat data for the PE and PP [1,8,9] are listed in Table 3.

The PE/PP composite, which was specifically prepared for this work by the manufacture of the material, was made from plastic waste material used as an ingredient of the PWFA composite. The PE/PP composite has a PE-to-PP ratio of 37:63, which

almost equals the PE-to-PP ratio of the PWFA composite. In this study, the granular sample, which had a grain size of not more than about 0.5 mm, was prepared.

The specific heat increased from 1.9 $kJ \cdot kg^{-1} \cdot K^{-1}$ to 2.5 $kJ \cdot kg^{-1} \cdot K^{-1}$ with an increase in temperature from 305 K to 360 K. The variation in the data for 5 $K \cdot min^{-1}$ was within ±3.5 %. The results for 2 $K \cdot min^{-1}$ agreed with those for 5 $K \cdot min^{-1}$ within 1 %. But the results for 10 $K \cdot min^{-1}$ were lower than those for 5 $K \cdot min^{-1}$. The variations of the data for 2 $K \cdot min^{-1}$ and 10 $K \cdot min^{-1}$ were within ±3 %. The specific heat value for the PE/PP composite was between the values for PE and PP.

The additivity rule is applied to the estimation of the specific heat of the PWFA composite c_{pw}, then the specific heat c_{pw} can be expressed using the following equation:

$$c_{pw} = c_p \Phi_p + c_{fa} \Phi_{fa} + c_{fr} \Phi_{fr} + c_g \Phi_g \tag{3}$$

where c and Φ are the specific heat and mass ratio of the components of the PWFA composite, respectively. The subscripts fa, fr, g, and p represent fly ash, fire retardant, glass fiber, and PE/PP composite, respectively.

The PWFA composite has a much lower content of the glass fiber than the other constituents, as illustrated in Table 1. Consequently, the term $(c_g \Phi_g)$ in Eq. 3 is ignored, and then the specific heat of the fire retardant c_{fr} can be estimated using the following equation:

$$c_{fr} = \frac{c_{pw} - \left(c_p \times \Phi_p + c_{fa} \times \Phi_{fa}\right)}{\Phi_{fr}} \tag{4}$$

Figure 7 shows the specific heats of the PWFA composite and its constituents. The specific heat of the fire retardant was calculated by Eq. 4, when the content of fire

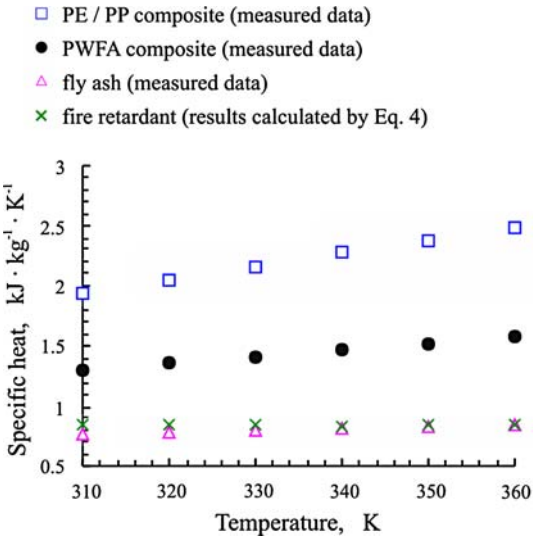

Fig. 7 Specific heats of PWFA composite and its constituents

retardant Φ_{fr} equals 0.17. The data for the PE/PP composite are the highest, and those for the fly ash are the lowest. The value for the PE/PP composite is at least 2.5 times higher than that for the fly ash. In contrast, the value for the fire retardant is as large as that for the fly ash. Therefore, the specific heat of the PWFA composite depends largely on the content of the plastic waste.

5 Conclusion

To obtain the specific heat of the PWFA composite and its components, the authors measured the specific heats of the PWFA composite, fly ash, and PE/PP composite using a differential scanning calorimeter and estimated the specific heat of the fire retardant. Then the following conclusions were obtained.

1. The specific heat of the PWFA composite increases from $1.25\,\mathrm{kJ}\cdot\mathrm{kg}^{-1}\cdot\mathrm{K}^{-1}$ to $1.59\,\mathrm{kJ}\cdot\mathrm{kg}^{-1}\cdot\mathrm{K}^{-1}$ with an increase in temperature from 305 K to 360 K.
2. The uncertainty for the specific heat data of the PWFA composite is estimated to be about 4 %.
3. The specific heat of the fire retardant is as large as that of the fly ash. In addition, the specific heat of the PWFA composite depends largely on the content of the plastic waste.

References

1. Japan Society of Thermophysical Properties, *Thermophysical Properties Handbook* (Yookendo, Tokyo, 1990), pp. 118–123, 260–261, 285–289, 583 [in Japanese]
2. J. Fujino, T. Honda, Measurement of thermal conductivity of recycled composite material of plastic waste and fly ash, in *Proceedings of the 7th Asian Thermophysical Properties Conference*, Hefei, China (2004)
3. *Instruction Manual for DSC22C System* (Seiko Instruments Inc., Chiba, 1994) [in Japanese]
4. Y.S. Touloukian, E.H. Buyco, in *Specific Heat: Nonmetallic Solids*, ed. by Y.S. Touloukian, C.Y. Ho. Thermophysical Properties of Matter, vol. 5 (IFI/Plenum, New York, 1970), pp. 24–29, 110–113, 202–206
5. *JIS K 7123 Testing Methods for Specific Heat Capacity of Plastics* (Japanese Standards Association, Tokyo, 1987)
6. American Society of Mechanical Engineers, *Measurement Uncertainty* (Japan Society of Mechanical Engineers, Tokyo, 1987) [Translated in Japanese]
7. Japan Fly Ash Association, *Coal Ash* (Japan Fly Ash Association, Tokyo, 2004) [in Japanese].
8. Japan Society of Mechanical Engineers, *JSME Data Book: Heat Transfer*, 4th edn. (JSME, Tokyo, 1986), p. 321 [in Japanese]
9. Society of Polymer Science, *Koubunshi Data Handbook* (Baifukan, Tokyo, 1986), pp. 20–21 [in Japanese]