MEASUREMENT OF THE SPECIFIC HEAT OF PLASTIC WASTE / FLY ASH COMPOSITE MATERIAL USING DIFFERENTIAL SCANNING CALORIMETRY

J. Fujino [1, 2] and T. Honda [1]

[1] Department of Mechanical Engineering, Fukuoka University,
Nanakuma 8-chome, Jonan-ku, Fukuoka 814-0180, Japan.

[2] Corresponding author. E-mail: fujino@cis.fukuoka-u.ac.jp

ABSTRACT

PWFA (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 trough which shields underground lines. However, there exists little information for the thermophysical properties of the composite. The fundamental data about the thermophysical properties and structure of the composite is required for discussing the heat transfer in the composite and creating the different proportion of the composite material.

The present paper deals with the measurement of the specific heat of the PWFA composite and its components using a differential scanning calorimeter. The composite sample, which ranged from 10 to 19 mg in mass, was cut out from a cable trough. The reference material was the sapphire disk of about 20 and 30 mg in mass. The constant heating rates were set at 2, 5 and 10 $K \cdot min^{-1}$. The temperature of the composite did not exceed 365 K to prevent the melting of plastic component.

The specific heat of the PWFA composite increased from 1.25 to 1.59 $kJ \cdot kg^{-1} \cdot K^{-1}$ with increasing the temperature from 305 to 360 K. The uncertainty for the data of the composite was estimated to be about ±4 %. The specific heat of the PWFA composite depends heavily on the content of the plastic waste.

KEY WORDS: composite material; DSC; fly ash; plastic waste; recycle; specific heat.

1. INTRODUCTION

PWFA (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. The irregular plastic in shape and size, different plastics and plastics unsuitable for recycle with an existing technology can be mixed in the ingredient of the composite. The composite can be recycled repeatedly. Currently, the composite is used for cable trough which shields underground lines. The thermal conductivity and specific heat of the composite is required to evaluate the heat transmitted through the cable trough and the temperature rise of the cable and cable trough because the temperature rise of the cable causes a serious problem. However, there exists little information for the thermophysical properties of the composite. The conventional theoretical models for the dispersed composite material were not applicable to the estimation of thermophysical properties because the thermophysical properties of fly ash and of the blended plastic formed of different plastics were not known [1].

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

The present paper deals with the measurement of the specific heat of the PWFA composite and its component using a differential scanning calorimetry. 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 data of the PWFA composite are described.

2. FEATURE OF THE PWFA COMPOSITE SAMPLE

A data on the composition of the PWFA composite specified by manufacture is listed in Table I. The plastic waste and fly ash components account for over 80 % of the total mass. Most of the recovered plastic wastes were the polypropylene and polyethylene resins used for the home wrapping materials. Fly ash was generated at the domestic coal-fired power plant. A small amount of glass fiber as reinforcement and a fire retardant is added in the ingredient of the PWFA composite. The name, chemical formula, composition and some other information of the fire retardant are undisclosed.

Figure 1 shows the observations of the particles of fly ash and the polished surface of the PWFA composite by a SEM and a metalloscope [2]. The specimen of the composite was cut out from a cable trough. The particles of fly ash were globular shape and under 60 μm in diameter. The round particles of fly ash disperse at irregular intervals as shown in Figure 1(b). Each particle of fly ash is surrounded by the matrix composed of the plastic waste and the fire retardant. The matrix is the continuous phase. Fly ash was mixed with the plastic waste and was heated until the melting temperature of the plastic waste. But the broken and deformed particles of fly ash could not be found. The PWFA composite is considered as a plastic composite material in which fly ash randomly disperses.

In order to measure the specific heat of the composite, the authors prepared the granular and thin sheet samples of the composite. The granular sample, which was grated, had a grain size of not more than about 0.5 mm. After the surfaces were polished with the sandpaper which has an abrasive particles size of about 9 μm, the size of the thin sheet sample was adjusted. The thin sheet sample had a size of about 2.5 ×2.5 mm^2 and a thickness of about 1 mm or less. The samples of the composite ranged from about 10 to 19 mg in mass.

3. MEASUREMENT METHOD

The specific heat was measured using a heat - flux differential scanning calorimeter [3]. The calorimeter is composed of a measuring device and a computer as the control and data acquisition devices. The computer can be used for the data analysis, too. The sensitivity of the calorimeter is 1.6 μW at the temperatures from -150 to 725 degrees Celsius.

Specimens, reference material and sample (test substance), were put into the separate aluminum capsule of 15 μℓ in capacity. The aluminum capsules ranged from 206.8 to 206.9 mg in mass. The capsule was sealed with a sealer.

The reference material was the sapphire disk of approximately 20 and 30 mg in mass. The mass of the specimen and the capsule was measured by the electric balance with the sensitivity of 0.01 mg. The uncertainty for the measurement of mass was estimated to be within ±1 %.

The measurement was carried out at the temperature of the PWFA composite sample not exceeding 365 K to prevent the melting of plastic component. The constant heating rates were set at 2, 5 and 10 $K \cdot min^{-1}$.

It is necessary to obtain the DSC curves of the empty capsule and capsules containing the specimen for evaluating the specific heat of sample. The DSC curves were obtained according to the following steps [3, 4]. Figure 2 shows the schematic diagram of the heat detecting element of the measuring device of the calorimeter

[3].

Step 1: Four clean empty capsules were prepared. One of them received the reference material. Another capsule received the sample. A content of other capsule was empty. All capsules were sealed with the sealer.

Step 2: The heating rate and the temperature range was inputted to the computer; i.e., the control program of temperature or the heating curve was fixed.

Step 3: An empty capsule was laid on the R-side capsule holder, as shown in figure 2. And another empty capsule was laid 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 reference material (which is called "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 "sample capsule" for short). As in the case of the empty capsule, the DSC curve of the sample capsule was measured.

During a series of the measurement, the authors never touched the empty capsule on the R-side capsule holder. And the displacement of the empty capsule did not happen. After the end of the measurements, the capsules kept in the apparatus and cooled by the natural cooling. The capsules were not displaced until the temperature of the capsule cooled down nearly the ambient temperature. By the measurements of procedure 3, 4 and 5, three DSC curves were obtained.

Figure 3 shows the experimental result of the DSC curves of the PWFA composite when the heating rate was set at 5 $K \cdot min^{-1}$. Symbol T is the temperature. And symbols Y_{ec}, Y_r and Y_s mean the DSC signals of the empty, the reference material and the sample capsules, respectively. The DSC signals changed transiently at the beginning and end of the rise of temperature. And the DSC signal varied linearly with increasing time or temperature except for the two periods of transient response. The DSC data except for the effects of the transient response was used for the calculation of the specific heat. The specific heat of the sample, c_s, is given by

$$c_s = \frac{M_r}{M_s} \times \frac{(Y_s - Y_{ec})}{(Y_r - Y_{ec})} \times c_r \qquad (1)$$

where c_r is the specific heat of reference material. And M_r and M_s are the mass of the reference material and the sample, respectively.

4. RESULTS AND DISCUSSIONS

Figure 4(a) shows the experimental results of the specific heat of the PWFA composite when the heating rate was set at 5 $K \cdot min^{-1}$. The specific heat was independent of the mass and shape of the PWFA composite sample, and increased with increasing the temperature, *T*. As shown in figure, a broken line represents the correlation line obtained from our measured data using the means of a least-square method. The measured data accorded with the correlation line was within ±3 %. In other words, the deviation of the data for 5 $K \cdot min^{-1}$ was within ±3 %.

The experimental results for the heating rate of 2, 5 and 10 $K \cdot min^{-1}$ are shown in figure 4(b). The distribution range of the data obtained for 2 and 10 $K \cdot min^{-1}$ were indicated, too. The experimental results for 2 and 10 $K \cdot min^{-1}$ were obtained using the same way for 5 $K \cdot min^{-1}$. The data for 5 $K \cdot min^{-1}$ agreed with those for 2 $K \cdot min^{-1}$ within 0.2 %. But the data for 10 $K \cdot min^{-1}$ were about 2 % lower than those for 2 $K \cdot min^{-1}$. The deviation of the data for 10 $K \cdot min^{-1}$ was within ±3 %. The recommended heating rate is perhaps 2 and 5 $K \cdot min^{-1}$ for the measurement of the specific heat of the PWFA composite. Taking into account the uncertainty for the measurement of mass and the deviation and reproducibility of the present data, the uncertainty for the specific heat data was estimated to be about ±4 % [5]. Based on the data obtained for 2 and 5 $K \cdot min^{-1}$, the specific heat of the PWFA composite can be expressed using the Eq. (2), at the temperatures of 305 to 360 K.

$$c_s = -0.47 + 0.0057 \times T \qquad (2)$$

Figure 5 shows the experimental results for the fly ash particles. The specific heat increased from 0.75 to 0.88 $kJ \cdot kg^{-1} \cdot K^{-1}$ with increasing the temperature from 310 to 385 K. The deviation of the data was within ±7 %.

Figure 6 shows the experimental results for the PE / PP (polyethylene / polypropylene) composite. The experimental results for 2 and 10 $K \cdot min^{-1}$ were obtained using the same way for the PWFA composite. The PE / PP composite, which was specifically prepared for this work, was made from the plastic waste used for the ingredient of the PWFA composite. The composite has a PE - PP ratio of 37 : 63, and almost equals the PE - PP ratio of the PWFA composite. The grain size of the grated composite sample was about 0.5 mm or less.

The specific heat increased with increasing the temperature. The deviation of the data for 5 $K \cdot min^{-1}$ was within ±3.5 %. The result for 2 $K \cdot min^{-1}$ agreed well with that for 5 $K \cdot min^{-1}$. But the result for 10 $K \cdot min^{-1}$ was lower than that for 5 $K \cdot min^{-1}$.

The specific heat of the PWFA composite can be expressed using the Eq. (3).

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

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

If the term ($c_g \times \Phi_g$) is ignorable and Φ_{fr} equals 0.17, the specific heat of the fire retardant, c_{fr}, is estimated using the Eq. (4).

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

Figure 7 shows the specific heats of the PWFA composite and its components. The data for the fire retardant was calculated by the Eq. (4). The data for the PE / PP composite is the highest and those for the fly ash is the lowest. The specific heat value of the PE / PP composite is at least 2.5 times higher than that of the fly ash. There is not so much of the difference in specific heat between the fly ash and the fire retardant. Thus, the specific heat of the PWFA composite depends heavily on the content of the plastic waste.

5. CONCLUSIONS

In order 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 the PE / PP composite using a differential scanning calorimeter and estimated the specific heat of the fire retardant. The following conclusions were obtained.

1. The specific heat of the PWFA composite increased from 1.25 to 1.59 $kJ \cdot kg^{-1} \cdot K^{-1}$ with increasing the temperature from 305 to 360 K.

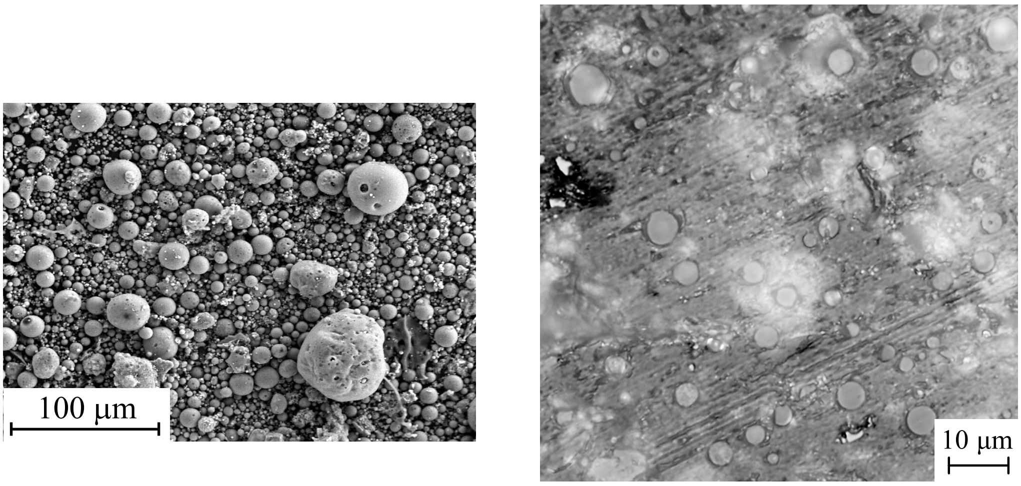
2. The uncertainty for the specific heat data of the PWFA composite was estimated to be about ±4 %.
3. The specific heat of the fire retardant is equivalent to that of the fly ash. And the specific heat of the PWFA composite depends heavily on the content of the plastic waste.

REFERENCES

1. Japan Society of Thermophysical Properties, *Thermophysical Properties Handbook* (Tokyo: Yookendo, 1990) 285 - 289 (in Japanese)
2. J. Fujino and 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 in China, 2004) on CD-ROM.
3. Seiko Instruments Inc., *Instruction manual for DSC22C system* (Seiko Instruments Inc., 1994) (in Japanese).
4. Japanese Standards Association, *JIS K 7123 Testing methods for specific heat capacity of plastics* (Tokyo: Japanese Standards Association, 1987).
5. American Society of Mechanical Engineers, *Measurement Uncertainty* (Tokyo: Japan Society of Mechanical Engineers, 1987) (Translated in Japanese).

Table I. Composition of PWFA composite.

<table>
<tr><th colspan="3">components</th><th>contents per unit mass (%)</th></tr>
<tr><td rowspan="3">plastic waste</td><td>polypropylene</td><td>62</td><td rowspan="3">45</td></tr>
<tr><td>polyethylene</td><td>36</td></tr>
<tr><td>other</td><td>2
sum: 100 %</td></tr>
<tr><td colspan="3">fly ash</td><td>38</td></tr>
<tr><td colspan="3">glass fiber</td><td>2</td></tr>
<tr><td colspan="3">fire retardant</td><td>15
total: 100 %</td></tr>
</table>



(a) fly ash: ×300 (by SEM) (b) PWFA composite: ×1000 (by metalloscope)

Figure 1. Observations of the particles of fly ash and the polished surface of the PWFA composite.

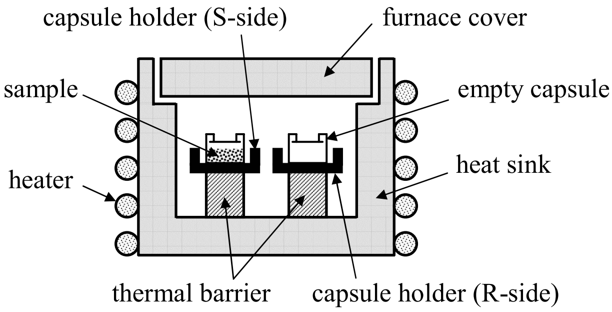


Figure 2. Schematic diagram of the heat detecting element of the measuring device of the calorimeter [3].

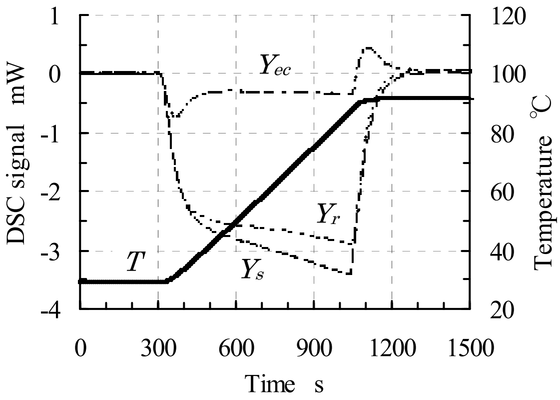
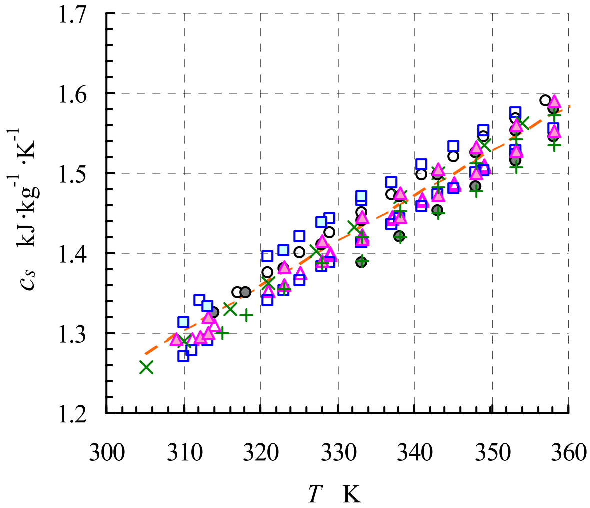


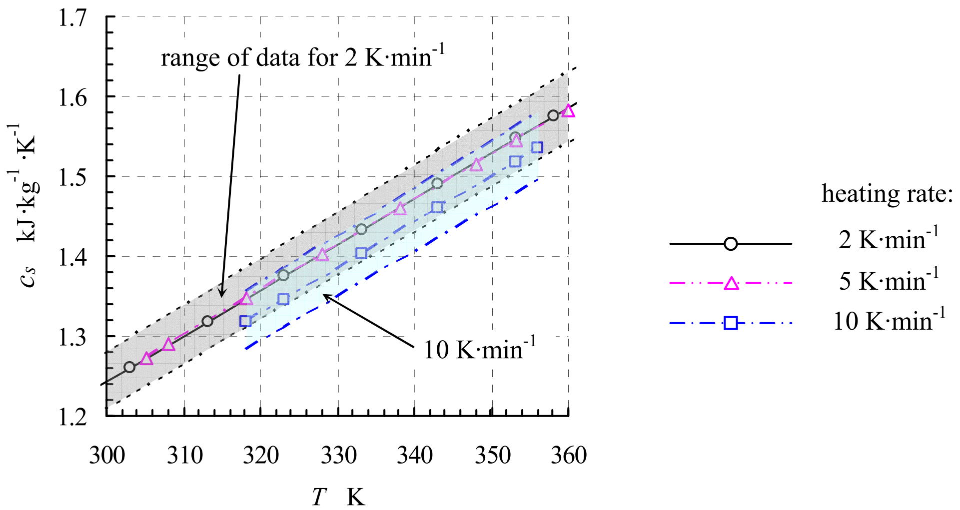
Figure 3. Experimental results of the DSC curves of the PWFA composite (T: temperature, Y_{ec}: DSC signal of the empty capsule, Y_r: DSC signal of the reference material capsule, Y_s: DSC signal of the sample capsule).



sym.	PWFA composite No.	PWFA composite mass (mg)	PWFA composite shape	sapphire disk mass (mg)
○	04- 3-12A	14.7	grains	29.6
△	04- 3-12B	18.7	grains	29.6
□	04- 4- 5A	15.3	grains	29.6
×	04- 4- 5B	10.2	grains	19.6
●	05- 4-26A	16.7	a thin sheet	29.6
▲	05- 4-26B	11.5	a thin sheet	19.6
■	05- 5-12A	11.0	a thin sheet	19.6
+	05- 5-12B	16.8	a thin sheet	29.6

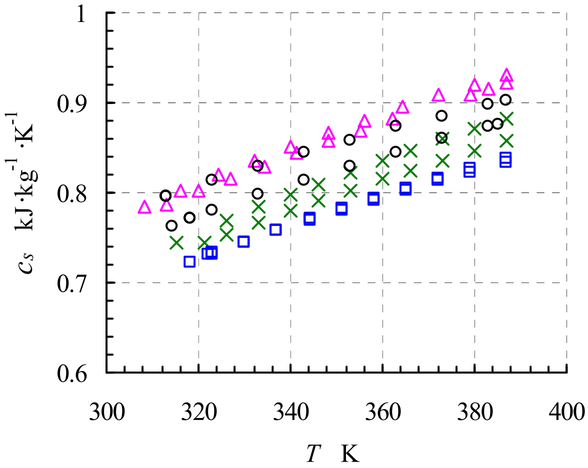
- - - - - correlation line for 5 K·min^{-1}

(a) In case of heating rate of 5 K·min^{-1}.



(b) Effect of the heating rate.

Figure 4. Experimental results for the PWFA composite.



sym.	Fly ash particles		sapphire disk
	No.	mass (mg)	mass (mg)
○	04- 4-28A	18.9	19.6
△	04- 4-14B	20.8	19.6
□	04- 4-28B	29.0	29.6
×	04- 4-14A	29.7	29.6

heating rate: 5 K·min^{-1}

Figure 5. Experimental results for the fly ash particles.

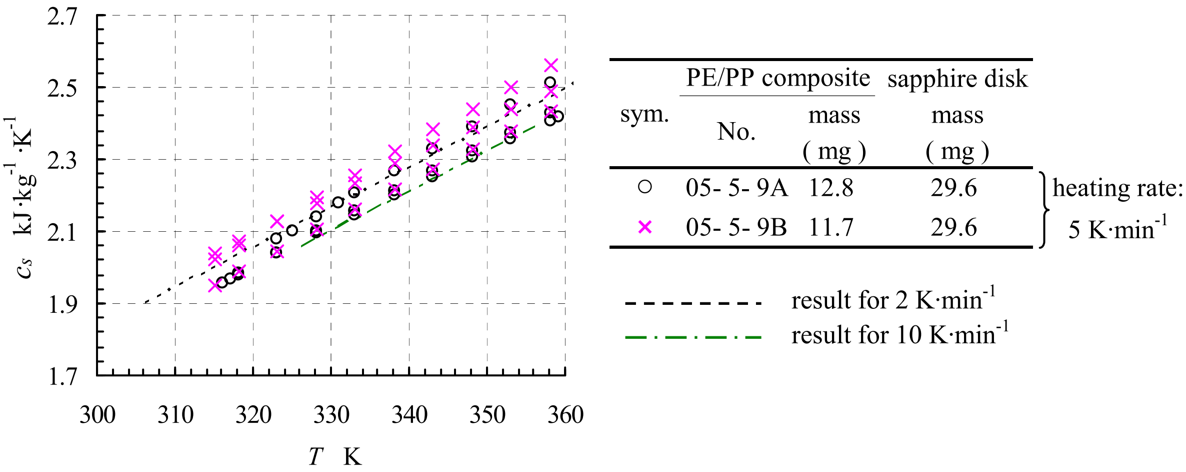


Figure 6. Experimental results for the PE / PP composite.

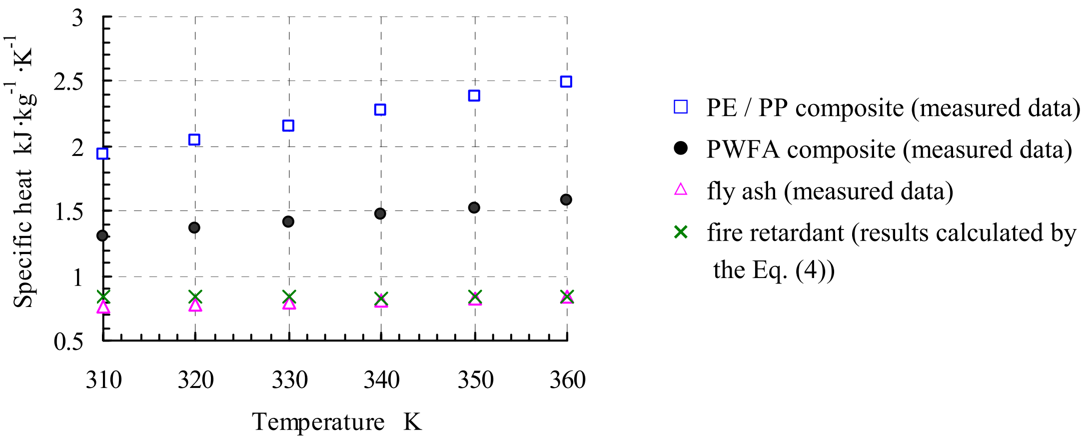


Figure 7. Specific heats of the PWFA composite and its components.