

Characterization of tea polyphenols as potential environment-friendly fire retardants

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Abstract. In this work we investigated the oxidation properties of tea polyphenols and their potential as the fire retardants. Two types of tea polyphenols were adopted, which were extracted from red tea and green tea leaves, respectively. Their macroscopic performance during pyrolysis and oxidation at elevated temperatures were examined by using a heating furnace. Mass change, heat evolution and gas products of tea polyphenols during heating in air were also monitored by using a thermo-gravimetric analyzer (TGA) integrated with a differential scanning calorimeter (DSC) in conjunction with online Fourier Transform Infrared Spectroscopy (FTIR) and mass spectroscopy (MS). A tea polyphenol sample first becomes a brown semi-fluid after heating, and gradually turns into highly-porous black chars with significantly expanded volume. By raising the temperature to ~550 °C at a rate of 10 °C/min, the mass of a sample reduces by nearly 70% to form a large quantity of inert gases that are mainly composed of H₂O and CO₂. It was found that the aerial oxidation products of tea polyphenols in the solid phase possess good heat insulation property; meanwhile, the substantial release of a lot of water and its evaporation during oxidation of tea polyphenols removes a large amount of heat from a sample located in a heating environment. The heat insulation of tea polyphenols may withstand up to 550 °C. The present work confirms tea polyphenols as potential superior and environment-friendly fire retardants.

1. Introduction

Fire retardancy of interior decoration materials has drawn increasing attention from the environmental safety sector because of the rising building fire incidents occurring in recent years. Steel products are widely used in the construction of high-rise and large-space buildings, which claims an urgent need for developing ultra-thin intumescent fire retardant coatings as part of fire protection measures[1, 2]. The improvement of the fire-resistant performance of the usual building materials, such as plywood and polymers is mainly achieved by the addition of organic or inorganic fire retardants. In the situation of a fire, such additives may be effective by triggering a specific fire retardant mechanism; however, heavy smoke and harmful even corrosive gases may accompany as a consequence, resulting in secondary pollution of the environment[3-5]. The development of more effective and environment-friendly fire retardants is of great importance to reduce the impact of fire incidents on the built environment and human's properties in case of a fire.

Tea polyphenols are natural products extracted from tea leaves and are widely used in food processing, health care and other industries because of their good antioxidant property[6, 7]. Existing



studies indicate that tea polyphenols can be classified as aromatic compounds rich in active phenolic hydroxyl groups[8]. When pyrolyzed in an inert atmosphere subject to linear heating[8], tea polyphenols retain antioxidant capacity at low and moderate temperatures, and generate large amounts of H₂O and CO₂, suggesting their potential as environment-friendly fire retardants. The remaining technical issues to be resolved here include the following: what is their performance by heating in air and undergoing the aerial oxidation and whether tea polyphenols could react as effective agents for fire isolation and retardancy.

In the present work, we investigated the oxidation behaviors of tea polyphenols and looked into the physical and chemical nature behind the phenomena observed. A tea polyphenol sample with specific thickness was heated by using a heating furnace to observe its performance during the oxidation process. By using a thermo-gravimetric analyzer (TGA) integrated with a differential scanning calorimeter (DSC) in conjunction with online Fourier Transform Infrared Spectroscopy (FTIR) and mass spectroscopy (MS), the thermal stability, heat evolution and gas production of a sample undergoing linear heating in an aerial atmosphere were monitored, which enables to analyze the variation of morphological structure and formation of products during heating and oxidation of tea polyphenols. On this basis, the potential of tea polyphenols as fire retardants was then assessed.

2. Experimental materials and test methods

Two types of tea polyphenols were obtained from Fuzhou Corona (Rimian) Science & Technology Development Co., Ltd. and Changzhou Yangsen Biology Science & Technology Co., Ltd, which were extracted from red tea and green tea leaves, respectively. They are in powder, and labelled as RM and YS samples. They were sealed and stored at the temperatures ~5 °C prior to use.

Proximate analysis of the samples was carried out by using a proximate analyzer (Sundy SDTGA 5000). After further milled, a sample weighed ~1 g was prepared for testing. The test results include the contents of moisture (MC), volatile matters (VM), fixed carbon (FC), and ash (ASH). Ultimate analysis of a sample was done by using an elemental analyzer (Elementar Vario Macro Cube). Samples were ground into fine powder by a mortar, and then weighed ~10 mg with tinfoil holder prior to testing. The measurements determine the contents of C, H, O, N, and S elements of the samples. Heating values of the samples were measured by using an adiabatic oxygen bomb calorimeter (Sundy SDC5051). This instrument has a temperature sensitivity of up to 0.0001 K, and the measurements were performed with oxygen at a purity of 99.995%. The samples for measurements were prepared in the form of dry powder, and had a mass of 0.5–1.0 g. The measurement results of proximate and ultimate analyses as well as the heating values of the samples are reported in Table 1.

Table 1. Results of proximate and ultimate analyses as well as the heating values of RM and YS samples on air-dried basis.

Sample	Proximate analysis (wt. %)				Ultimate analysis (wt. %)					Heating values (MJ/kg)	
	MC _{ad}	VM _{ad}	FC _{ad}	ASH _{ad}	C _{ad}	H _{ad}	O _{ad}	N _{ad}	S _{ad}	Q _{gr,v,ad}	Q _{net,v,ad}
RM	4.04	64.97	30.91	0.08	54.78	4.15	36.74	0.20	0.01	21.04	19.25
YS	3.46	66.50	29.72	0.32	59.18	4.23	31.15	1.46	0.20	20.79	19.22

Oxidation performance of tea polyphenols was monitored by heating in air with assistance of a black crystal furnace (POVOS PL02). The power of the furnace was set at 2000 W with the temperature of the heating elements being between 575 and 600 °C. The process of pyrolysis and oxidation was monitored by videotaping with a JVC video camera (GC-PX10AC) installed on a tripod. Prior to a test, the powder of tea polyphenols was uniformly dispersed in a stainless steel ring with an internal diameter of 17.38 mm and a height of 1.94 mm. A test was commenced by placing the sample tray at the center of the furnace and switching on the power of the furnace. The test was finished, after the sample completely stopped exhibiting any physical changes. The thermal conductivity of tea polyphenol powders and their oxidation products in solid phase were measured by using a thermophysical property analyzer (Hot Disk TPS-2500 S). During a measurement, the equilibrium

temperature of the instrument was set to 25 °C, and the heating power was set at 3 W along with the test period of 20 s.

Mass change of a sample undergoing heating at air atmosphere was measured by using TGA/DSC (Netzsh STA449F3), and the gas evolution was traced by an on-line FTIR (Bruker VERTEX70V) in conjunction with a MS instrument (Netzsh QMS403C). The measurements were carried out by using the oxygen and argon bottles with a purity of 99.999% at the flow rate of 80 mL/min. The samples for measurements were prepared in the form of fine powder, and had a mass of ~30 mg. During a measurement, a sample was balanced at the temperature of 35 °C, and then was heated to 800 °C at the heating rate of 10 °C/min. Test results were recorded in the generated data files.

3. Results and discussion

3.1. Performance of tea polyphenols by heating in air

As shown in Table 1, the contents of moisture, volatile matter and ash of tea polyphenols are all lower than those of usual biomass materials, whereas the content of fixed carbon of tea polyphenols maintains at ~30%, which is higher than that of usual biomass. The tea polyphenols essentially comprise C and O elements, and the combination of which constitutes >90% of the total elemental contents. They contain minor amount of N element, whereas the content of S element is almost zero. Thermal conductivity of RM and YS samples was found to be 0.081 W/(m·K) and 0.087 W/(m·K), respectively, claiming that they can be classified as the thermal insulation materials (i.e. thermal conductivity ≤ 0.12 W/(m·K))[9].

The performance of a tea polyphenol sample during pyrolysis and oxidation was tested by heating in air using a black crystal furnace at a power of 2 kW. Typical observation results for these two types of samples are shown in Figure 1. For a RM sample, we observed that its morphologic appearance gradually changed from brown red powder to sticky dark brown semi-fluid and eventually turned into highly porous black char-like products in general. The sample volume continuously increased by heating. The top of the sample was covered with a transparent brown-coloured substance, which rose with the expansion of the sample volume. The sample finally stopped its volume change with a clear brown surface presented at the top.

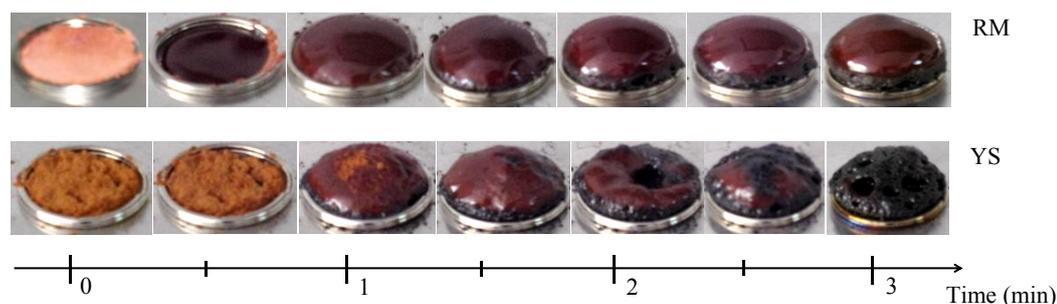


Figure 1. Performance of RM and YS samples by heating in air.

Pyrolysis and oxidation of the YS sample were similar to those of the RM sample when placed in the same heating environment. However, the time required for a YS sample to turn into a brown semi-fluid was longer compared with that for a RM sample, and the YS sample was completely converted into porous black chars at the end of the test. As exhibited in Figure 1, the volume of the YS sample swelled rapidly soon after heating, and gradually collapsed with small holes appearing on its top surface; Followed by healing of the surface holes, the volume of the sample began to increase rapidly again. After several rounds of up and down in the sample volume, the sample eventually stabilized.

No any obvious signs of combustion or smoldering appeared on the surface of the samples during exposure to the set heating environment for nearly 300 s. Analysis of the solid residues of the two samples after the tests indicated that these solid products are chars with very high porosity, and their thermal conductivity is close to that of air (0.023 W/(m·K)) by preliminary measurements and the

associated estimation. By monitoring the temperature variation of tray surface (i.e. the sample base) using a K-type thermocouple with a joint diameter of 0.54 mm, we confirmed that the tray temperature continuously rises while heating, and finally stabilizes at ~ 550 °C throughout the test.

3.2. Mechanistic analysis of tea polyphenol oxidation

The mass change and heat evolution of a sample were measured by heating in aerial atmosphere using TGA/DSC techniques, and the simultaneous gas evolution was traced by an on-line FTIR in conjunction with a MS system. The sample temperature was raised up to 800 °C at a rate of 10 °C/min, and the measurement results are shown in Figures 2 to 4. It is evident that the variation trends of mass loss and the heat flow rates of these two types of tea polyphenols are similar to each other (refer to Figure 2). During the process of linear heating, we observed three distinct mass loss stages, corresponding to three peaks appeared on the mass loss rate curves. The first stage of mass loss occurs at the temperatures <200 °C, highlighting the phenomena of evaporation of free water and bound water stored in the sample. Starting at ~ 200 °C, the sample mass continuously drops towards 350 °C, which accounts for 29% of total mass loss with mass loss rate curve forming a narrow but sharp peak. The maximum mass loss rate occurs at about 240 °C. The third stage of mass loss takes place at 350–570 °C. The sample undergoes a second process of rapid decrease in mass with a broad and high mass loss rate peak formed. This stage accounts for 66% of total mass loss, and the maximum mass loss rate occurs at ~ 490 °C. The sample mass tends to level off after 570 °C.

It is seen that the heat flow rates are always negative below 200 °C, specifying continuous endothermal reactions occurring at this stage. With the temperature increase, the heat flow rates increase progressively, and increase rapidly at about 400 °C. After reaching the maximum at ~ 500 °C it drops and eventually decreases to 0 at approximately 570 °C.

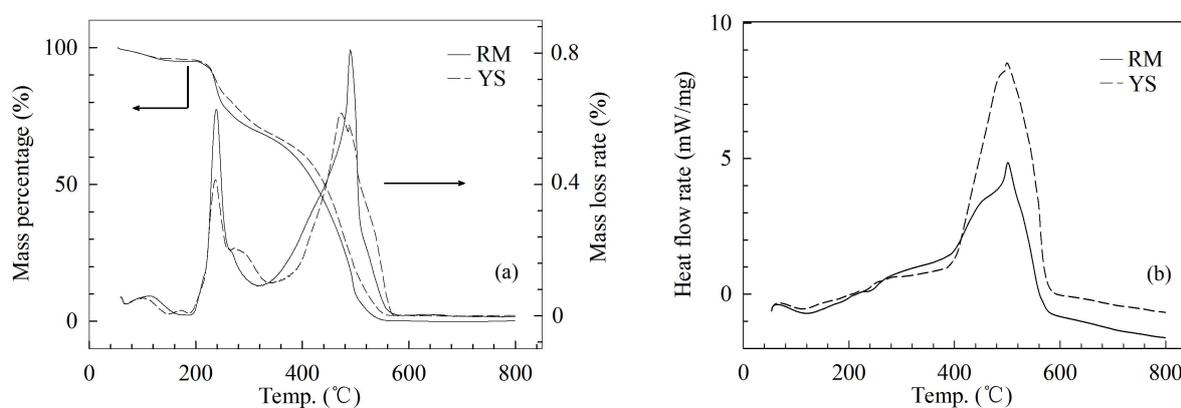


Figure 2. Mass change and mass loss rates (a) as well as heat flow rates (b) of RM and YS samples observed during the oxidation measurements.

The infrared absorption intensities of gas products effluent during the oxidation process are shown in Figure 3, with the time axis being replaced by the linearly-increased sample temperatures throughout the synchronous thermogravimetric test. The FTIR data indicate that the major gas products at the oxidation process of tea polyphenols are H₂O (3400–3200 cm⁻¹) and CO₂ (2400–2220 cm⁻¹). Minute amounts of organic matters (1700–700 cm⁻¹) were observed, including acids (–COOH), alcohols (–OH), alkanes (C–C), and ethers (C–O–C). The shoulder-like small absorption peak represented CO, and gradually vanished at high temperatures. This phenomenon could be attributed to CO being easily oxidized at elevated temperatures.

The gas evolution trends observed are in consistent with the synchronous mass spectrum signals observed for H₂O and CO₂, as displayed in Figure 4. Because of the weak signals detected in ion current intensity, the results of the other gas species are not reported here. The release patterns of H₂O and CO₂ have a close relationship with the mass change of the samples, as obtained by the thermo-

gravimetric analysis. At the second stage of mass loss (200–350 °C), the ion current intensities of H₂O and CO₂ undergo significant increase and then level off with an increase in temperature. At the third stage of mass loss (350–570 °C), the ion current intensity for H₂O decreases, whereas the intensity of ion current of CO₂ keeps increasing considerably and then drops after reaching a peak. In light of the similar patterns of the peaks presented for the ion current intensity of CO₂ and the mass loss rate curve, we expect that the amounts of CO₂ produced at the third stage are reasonably large.

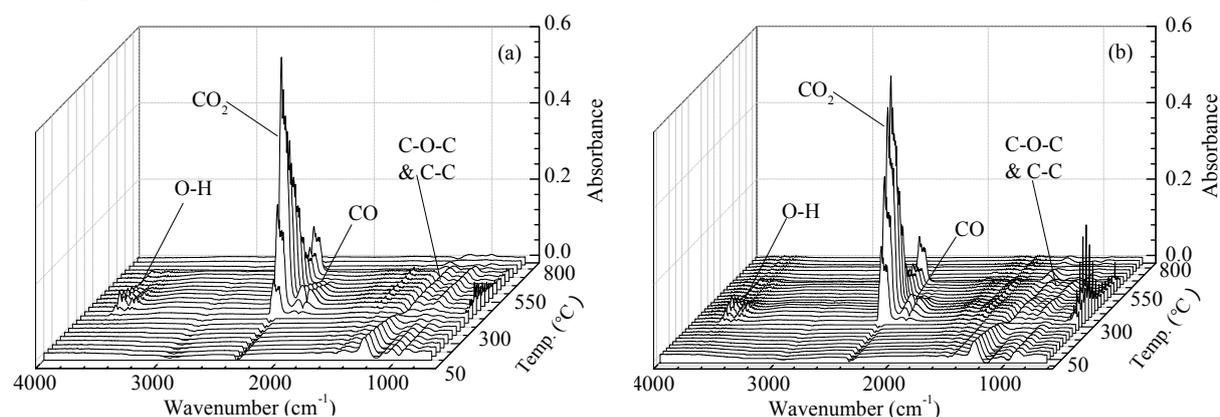


Figure 3. FT-IR spectra of effluent gases collected during the oxidation measurement of RM (a) and YS (b) samples.

These outcomes can be applied to explain the macroscopic oxidation phenomenon observed for tea polyphenols after heating. A tea polyphenol sample quickly reached the viscosity flow temperature after heating, and then became semi-fluid with high viscosity[10], which has mobility and good ductility to a certain extent. At the same time, tea polyphenols began to experience three stages of mass loss, accompanied by the release of large amounts of H₂O and CO₂. The process of releasing the large amounts of gas products through pyrolysis and oxidation pushed such semi-fluids to extend around, enabling to expand the volume of a tea polyphenol sample. With the temperature further increasing, the semi-fluid was eventually converted into chars, which possessed a stable structure and fixed volume[11, 12]. Hence, the oxidation products of tea polyphenols in solid phase had a loose and porous structure.

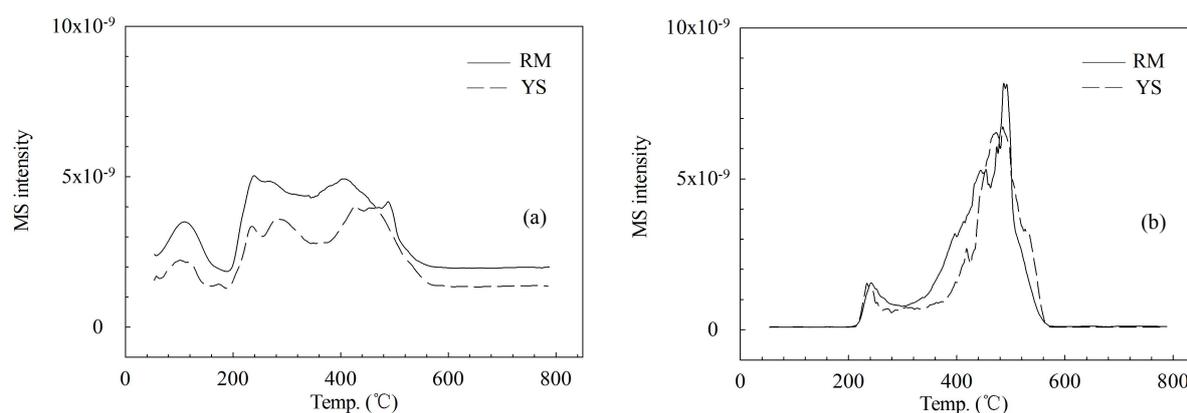


Figure 4. The variation of ion current intensities of effluent gases detected for RM and YS samples; (a) H₂O, (b) CO₂.

A tea polyphenol sample at the bottom that is in contact with the surface of the furnace, first entered the stage of mass loss, whereas the upper layer of the sample remained at the semi-fluid status due to low heat conductivity of the tea polyphenols. By forming a sealed space inside a sample, the gaseous products generated from the bottom of the sample created the pressure to expand the volume

of the sample. With the increase in temperature, more and more tea polyphenols began to decompose and oxidize to build up the internal pressure. When the internal pressure eventually pierced the surface of the semi-fluid on the top of the sample, the internal gas pressure was released, and the volume of tea polyphenol began to decrease (as displayed by a YS sample). However, the semi-fluid on the top may heal the pores on the surface due to its liquidity, causing the tea polyphenol sample to begin another round of volume expansion. After several rounds of volume variation, the sample was completely transformed into the chars with stable volume, which declared the conclusion of the sample pyrolysis and oxidation processes.

3.3. Potential fire retardant property of tea polyphenols

The volume of a tea polyphenol sample expanded by 5–6 times during oxidation, reflecting good ductility and the feature of liberating a large quantity of gas products of tea polyphenols after heating. It took several minutes for a tea polyphenol sample with a thickness of 1.94 mm to stop its physical change even at the temperatures as high as 550 °C, and the thermal conductivity measured for the solid oxidation residues is quite low (~ 0.036 W/(m·K)), which ensure the property of tea polyphenols as good heat insulator during pyrolysis and oxidation of tea polyphenols. In case of a fire, the rapid expansion of tea polyphenols would enable to increase the distance of heat transfer between the fire source and the materials to be protected; meanwhile, the oxidation products of tea polyphenols in solid phase could also create a protective layer with good heat insulation, which significantly reduces the level of external radiation heat flux impacted onto the materials to be protected. In addition, during linear heating, a tea polyphenol sample undergoes progressive oxidation towards a temperature up to 550 °C, which makes it possible for tea polyphenols to provide extended protection from a fire.

For usual biomass fuels, big differences can be seen in the mass change curves and the associated heat flow rate data obtained by the pyrolysis and aerial oxidation measurements, highlighting parallel reaction mechanisms occurring in the pyrolysis and oxidation processes[13]. In comparison with the results measured during the pyrolysis of tea polyphenols[8], the mass change and heat flow rate curves both in pyrolysis and oxidation processes were much closer at the temperatures <350 °C, indicating that tea polyphenols may undergo similar reactions either in air or in nitrogen. Tea polyphenols have demonstrated unique anti-oxidation features, especially at low temperatures[8]. Once tea polyphenols are painted on the surface of the materials to be protected, they are able to serve as anti-oxidation agents with effectiveness.

Tea polyphenols are capable of releasing large amounts of H₂O and CO₂ throughout the oxidation process. It is well known that the evaporation of H₂O takes away considerable heat. In industries, Mg(OH)₂ is widely used as a flame retardant additive, and the major retarding mechanism is the removal of heat by generating H₂O. The Mg(OH)₂ with a quantity of 100 g can remove the heat of about 85.9 kJ during its oxidation[14]. The H element in tea polyphenols was fully converted to H₂O during combustion. Therefore, based on the proximate and elemental analysis data of tea polyphenol samples, we found that every 100 g of tea polyphenols can release about 41 g of H₂O throughout the oxidation process, implying a removal of 92.5 kJ through evaporation. As a result, tea polyphenols have good capability to prevent heat absorption of a material from a fire source. In addition, a large amount of CO₂ produced by the pyrolysis and oxidation of tea polyphenols plays a role in isolating the combustible gases generated by the material from oxygen and subsequently slowing down the combustion reactions.

The conventional inorganic fire retardants are usually activated by following a certain retarding mechanism because of their simple chemical structures. For example, halogen-based fire retardants are mainly used for the release of non-flammable gases for flame retardancy, whereas phosphorus-nitrogen fire retardants generate carbon foams to build up heat insulation layers and oxygen barriers[15]. As for tea polyphenols, they generate a large amount of inert gases by heating; in the meantime, their features of rapid volume expansion and subsequent heat insulation can effectively reduce the heat transfer between the fire source and the materials to be protected. Thus, tea polyphenols are undoubtedly highly comprehensive in terms of their fire retardant mechanisms.

Conventional inorganic fire retardants usually work at low and moderate temperatures of below 400 °C. At higher temperatures, they could be completely oxidized. As tea polyphenols have a broad oxidation temperature range and an extended oxidation period, we could expect that tea polyphenols are able to greatly improve the applicable temperature range and retarding effects as fire retardants. Worthy of mentioning, the conventional inorganic fire retardant additives may generate significant amounts of smoke and poisonous gases during heating, which could result in secondary pollution of the environment. In contrast, tea polyphenols possess the environment-friendly features to release non-toxic gaseous oxidation products served as fire retardants. By taking into account the characteristics of their fine particle sizes and good decoration performance, tea polyphenols have great potential to be developed into new type of intumescent fire isolation and retardant coating materials.

4. Conclusions

It was observed that a tea polyphenol sample first becomes semi-fluid and gradually turns to highly-porous black chars with the volume significantly expanded during its heating from the ambient temperature to ~550 °C in air. No any obvious signs of combustion or smoldering appear on the sample surface. Measurements showed that the thermal conductivity of oxidation residues of tea polyphenols is close to that of air, highlighting their good heat insulation property. Mass change, heat evolution and effluent gases of the samples measured during aerial oxidation at elevated temperatures demonstrated that the samples undergo drastic mass loss, resulting in considerable gas evolution at the temperatures up to 550 °C. The gas products were found to comprise H₂O and CO₂ in principal.

It was concluded that tea polyphenols have more comprehensive properties in heat insulation and fire retardancy, in comparison with those conventional inorganic fire retardants. Commenced at the temperature of 200 °C, the tea polyphenols maintain their capability as heat insulators and fire retardants at the temperatures up to ~550 °C, suggesting their broad active temperature range as heat insulators and fire retardants. By taking into account the characteristics of their fine particle sizes and good decoration performance in practice, tea polyphenols prove to have great potential to be developed into new environment-friendly intumescent fire isolation and retardant materials.

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