EFFECTS OF FABRICATION PARAMETERS ON THE OXIDATION RESISTANCE OF WOOD/PHENOLIC RESIN CARBON COMPOSITES

VPLIV PARAMETROV IZDELAVE NA OKSIDACIJSKO ODPORNOST OGLJIKOVIH KOMPOZITOV NA OSNOVI LESA IN FENOLNE SMOLE

Yubo Tao, Peng Li^{*}

College of Material Science and Engineering, Northeast Forestry University, no. 26 Hexing Road, Xiangfang District, Harbin 150040, Heilongjiang, China

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The oxidation resistance of wood/phenolic-resin carbon composites (woodceramics) in air was investigated from room temperature to 700 °C by the simultaneous thermogravimetry and differential scanning calorimetry (TG-DSC) analysis. The elementary analysis, Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) were utilized to characterize the woodceramics samples prepared with different weight ratios of wood powder to phenolic resin (PF) and carbonized under 800 °C, 1000 °C, and 1400 °C. The elementary analysis revealed that the higher carbonization temperature contributed to a higher carbon content, whereas the higher ratio of PF led to a lower carbon content in the samples. The FTIR results showed that the higher carbonization temperature was beneficial to a more regular carbon structure, which was further proven by XRD. The TG-DSC analysis demonstrated that the oxidation resistance of woodceramics under a higher carbonization temperature. However, the increased ratio of PF did not bring apparent improvements to the oxidation resistance of the samples. The apparent activation energy was high at the intial reaction stage, and then decreased with the development of thermal degradation, which indicated that more energy was consumed for the completion of the oxidation reactions at the start stage. This study showed that the developed woodceramics exhibited good oxidation resistance in air below 300 °C.

Keywords: woodceramics, oxidation resistance, TG, DSC

Avtorja opisujeta raziskavo oksidacijske odpornosti ogljikovih kompozitov na osnovi lesa in fenolne smole (angl.: woodceramics) na zraku pri sobni in povišanih temperaturah (do 700 °C). Pri tem sta uporabila simultano termogravimetrijo in diferencialno vrstično kalorimetrijo (TG-DSC). Vzorce kompozitov sta pripravila z različnim masnim razmerjem lesnega prahu in fenolne smole (PF). Karbonizacijo (pooglenitev) vzorcev sta izvedla pri 800 °C, 1000 °C in 1400 °C. Za karakterizacijo vzorcev kompozitov sta uporabila elementno analizo, Furierjevo transformacijsko infrardečo spektroskopijo (FTIR) in rentgensko difrakcijo (XRD). Elementna analiza je pokazala, da višja temperatura karbonizacije prispeva k višji vsebnosti ogljika, medtem ko višji delež PF v kompozitu privede do manjše vsebnosti ogljika v vzorcih. Rezultati FTIR spektroskopije so nedvoumno pokazali, da višja temperatura karbonizacije prispeva k bolj urejeni strukturi ogljika. To je bilo potrjeno tudi z XRD. TG-DSC analiza je pokazala, da odpornost kompozita proti oksidaciji narašča z naraščajočo temperaturo karbonizacije, kar je posledica popolnejšega razvoja grafitizacije kompozita pri višjih temperaturah karbonizacije. Po drugi strani povečanje deleža PF v kompozitni mešanici ni prispevalo k izboljšanju oksidacijske odpornosti vzorcev. Navidezna aktivacijska energija je bila visoka v začetnem stadiju reakcij in se je zmanjševala z razvojem termične degradacije. To nakazuje, da je več energije porabljene za dokončanje reakcij oksidacije v začetnem stadiju. Študija je pokazala, da je razviti kompozit na osnovi lesa in PF dobro obstojen proti oksidaciji do 300 °C.

Ključne besede: lesna keramika, odpornost proti oksidaciji, TG, DSC

1 INTRODUCTION

Biomass and resin hybrid carbon composites, i.e., woodceramics, are environmentally friendly, light weight, and low cost. Woodceramics are usually obtained through impregnating resin into wood or woody materials, and then carbonizating in vacuum conditions at high temperatures.^{1–3}

Woodceramics possess unique characteristics such as high wear and friction resistance,⁴ electromagnetic shielding capacity,⁵ and good mechanical properties.⁶ Previous studies show that porous woodceramics have

lptyb@aliyun.com

and porous structure.⁷⁻¹⁴ The unique three-dimensional natural microstructure of wooderamics cannot be artificially fabricated easily. Moreover, woodceramics have hierarchical pores structures tunable in the micropore-to-macropore range. Pan et al. proved that the sugarcane bagasse woodceramics demonstrated a hierarchical porous structure from the micrometer (0.6–21 μ m) to the nanometer scale (3.1–9.3 nm).¹⁴ As reported by Yang et al., these hierarchical pore structures were extremely useful in terms of mass transfer and enhancing the reaction pathways, and were anticipated to be effective catalyst media.¹²

potential applications for catalyst supports, gas filtration, brake pads, etc. due to their hierarchical, biomorphic,

^{*}Corresponding author e-mail:

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However, as functional materials, the performances of woodceramics are usually determined by the materials' ability to resist heat. For example, catalytic reactions involving oxidizing conditions above 250 °C burned off carbon-supported catalysts and reduced its lifespan.¹⁵ Therefore, the thermal reactivity in air at high temperatures is a crucial characteristic to evaluate woodceramics' proper utilization as catalyst supports for durable applications. Ozao et al. analysed the thermal properties of apple woodceramics and their results showed that the higher carbonization temperature benefited the oxidation resistance of woodceramics.² Oishi et al. reported that the thermal degradation of woodceramics was dependent on the oxygen concentration.¹⁶

In this paper, to clarify the effects of the processing parameters on the characteristics as well as the oxidation resistance of woodceramics in air, the performances of wood flour/PF woodceramics were investigated using simultanous TG-DSC analysis from room temperature to 700 $^{\circ}$ C.

2 EXPERIMENTAL PART

2.1 Woodceramics preparation

The woodceramics were prepared using a laboratory-made fir powder and laboratory-synthesized PF resin. The fir powder used had a moisture content of 8 % and a size passing through a 40-mesh sieve. The PF resin had a solid content of 48–50 %, a viscosity of 30–40 s (TU-4 viscometer), an alkali content of 2.0–2.7 %, bromides of 16–24 %, and a storage period of at least 60 d at 5–20 °C.

The composite preform was fabricated by impregnating PF resin into wood powder. The weight ratios of wood powder to PF resin were 40:60, 50:50 and 30:70. The procedures were conducted in three steps, i.e., drying, cold-pressing, and hot-pressing. Samples were then carbonized at temperatures 800 °C, 1000 °C, and 1400 °C in a vacuum sintering furnace under the heating rate of 2 °C/min.

2.2 Sample characterization

Before the thermal analysis, the samples were analyzed to determine the properties that may affect the thermal degradation abilities. The contents of C, H, and N of the dried samples were investigated by the CHNS-O Elemental Analyzer (Euro EA 3000-Eurovector Italy) with a combustion temperature at 1020 °C. The FTIR analysis was used to analyze the possible chemical functional groups in the samples using a Nicolet Magna 560 at a resolution of 4 cm⁻¹. The physical characteristics of the prepared woodceramics were identified by the X-ray diffraction (XRD) method on a Rigaku D/max-RB 12KW X-ray Diffractometer (Rigaku Corporation, Japan) using the nickel-filtered Cu-K_a radiation in the range of 2θ (10°–90°), where the scanning speed was 2 degree/min.

2.3 TG-DSC analysis

The TG-DSC analysis of ca. 10 mg dried material was performed under an air atmosphere in a TG-DSC OLAP analyzer (Netzsch Sta 449c, Deutschland, Germany) with the sensitivity of 0.1 μ g and 0.1 °C. The samples were heated from 25 °C to 700 °C in a Pt-Rh crucible. The air flow rate was 30 mL/min throughout the whole procedure. The test conditions are shown in **Table 1**.

Table	1.	Test	conditions	of	woodcera	mic	specimens
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Sample number	Weight ratios of wood powder to PF	Carbonization temperature (°C)	Heating rates of TG/DSC (°C/min)
S1	40:60	800	2
S2	40:60	800	5
S 3	40:60	800	10
S4	40:60	800	20
S5	40:60	1000	10
S6	40:60	1400	10
S7	50:50	800	10
S 8	30:70	800	10

2.4 Calculation of activation energy of thermal decomposition reaction

Using the data of TG, the conversion rate of the samples at any given time/temperature can be obtained with Equation (1):

$$\alpha = \frac{(m_0 - m_1)}{(m_0 - m_f)} \tag{1}$$

where, α : conversion rate; m_0 : initial sample weight; m_1 : sample weight at any given time; m_f : stable sample weight at the end of reaction.

It is assumed that the woodceramics are reactive substances, and the Arrhennius equation could be used to describe the reaction law of the thermal decomposition.

$$\beta = \frac{d\alpha}{dT} = A \exp\left(-\frac{E}{RT}\right) (1-\alpha)^n \tag{2}$$

where, β heating rate, K s⁻¹; α conversion rate; *T* temperature of sample, K; *A* prefactor; *E* apparent activation energy, J/mol; *R* gas constant, 8.314 J/mol·K; *n* reaction order.

In order to analyze the kinetic parameters of woodceramics, the apparent activation energy of woodceramics is able to be calculated using four heating rates with the Ozawa method.¹⁷

The TG data curves obtained at heating rates of (2, 5, 10, and 20) °C/min and Equation (3) were used in calculation.

$$\log\beta + 0.4567 \frac{E}{RT} = Const.$$
(3)

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If the weight loss rate of formula (3) is a constant, the heating rates β_1 , β_2 , β_3 , and β_4 correspond to the temperature T_1 , T_2 , T_3 and T_4 respectively. A straight line can be drawn using the data of 1/T and log β . The apparent activation energy *E* value can be obtained by calculating the slope of the straight line.

3 RESULTS AND DISCUSSION

3.1 Element analysis of woodceramics

The contents of C, H, and N of woodceramics under different carbonization temperatures as well as different ratios of wood powder to PF were presented in Table 2. As seen, the main component in all samples was carbon. The hydrogen content was low because H₂O, low molecular weight phenolic substances (LMP), and the low molecular weight hydrocarbon (LMH, including CH₄) were produced during the carbonization process.¹⁸ With the increase of the PF ratio, the carbon content of samples prepared under 800 °C declined slightly (S7, S3, and S8) along with lower H and N contents. However, under the same weight ratio of wood powder to PF (S3, S5, and S6), the increased carbonization temperatures contributed to higher carbon contents and lower amounts of heteroatoms. The increase of the carbon content and decrease of the oxygen content with the rise of carbonization temperature revealed that more energy was consumed to deprive the oxygen-containing functional groups.

Table 2: C, H, and N contents of woodceramincs

Sample number	Carboni- zation tem- perature /°C	Weight ratio of wood pow- der to PF	C/%	H/%	N/%	O + ash /%
S7	800	50:50	91.6	0.7	1.5	6.2
S3	800	40:60	90.2	0.6	1.4	7.8
S8	800	30:70	88.3	0.6	1.2	9.9
S5	1 000	40:60	95.9	0.2	1.4	2.5
S6	1 400	40:60	99.5	0.0	0.0	0.5



Figure 1: FTIR spectra of woodceramics at different carbonization temperatures (weight ratio of wood powder to PF is 40:60)

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Figure 1 shows the FTIR spectra of woodceramics obtained at 800 °C, 1000 °C, and 1400 °C, respectively. All the samples displayed a broad O-H stretching vibration at around 3 430 cm⁻¹. Meanwhile, the aromatic and aliphatic C-H asymmetrical stretching vibrations around 3000 cm⁻¹ exhibited a weak trend. C=O stretching vibrations between 1750 cm⁻¹ and 1700 cm⁻¹ disappeared with the deprival of oxygen in the samples. A symmetrical peak at 1629 cm⁻¹ was attributed to aromatic C=C in-plane stretching vibration.⁶ Strong absorptions at 1400 cm⁻¹ were the results of aromatic stretching vibrations and -CH₃ stretching resulted in peaks at 1384 cm⁻¹.^{18,19} Nevertheless, the vibration strengths of the C=C and -CH₃ stretching were lowered when the carbonization temperatures were increased. This phenomenon was assocaited with the deprival of low-molecular-weight substances and the diminished carbon and hydrogen contents, as described in Table 2.

Figure 2 presents the XRD intensity curves for the samples prepared under three carbonization temperatures. Two main and a weak wide peaks were detected over the scattering range. The peaks at around 22°, 43°, and 80° correspond to the (002), (10), and (11) peaks, which represented the graphite-like crystalline structure in woodceramics.6 The observed broad peaks illustrated the weak regularity of carbon in woodceramics. Furthermore, the data indicated that the amorphous carbons derived from wood powder and PF resin were hard to be graphitized. However, as the carbonization temperature increased, the (002) peak became sharper and moved to a larger angle slightly. It was shown that the higher carbonization temperature contributed to higher levels of graphitization and lower remaining content of the amorphous carbon.20,21

Figure 3 shows the curves of woodceramics prepared with different weight ratios of wood to PF. The contribution of PF content to the graphitization of woodceramics was not obvious. The research conducted by Qian et al. obtained similar results.⁶ Therefore, it can be concluded that carbonization temperature is the vital factor



Figure 2: XRD patterns of woodceramics carbonized under different temperatures

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Figure 3: XRD patterns of woodceramics carbonized at 800 $^{\circ}\text{C}$ (with different weight ratios of wood to PF)

to improve the regularity and crystallite growth of woodceramics.

3.2 Carbonization temperature vs. oxidation resistance

Figure 4 depicts the effects of carbonization temperatures 800 °C, 1000 °C, and 1400 °C on the oxidation resistance of woodceramics. The key data of TG from **Figure 4** were summarized and are listed in **Table 3**.

 Table 3: Oxidation resistance of woodeceramics under different carbonization temperatures

Sample number	Temperature at 9 % weight loss (°C)	Temperature at a starting of linear variation (°C)	Residual weight at 700 °C (%)
S3 (800 °C)	400	430	22.8
S5 (1000 °C)	565	600	60.9
S6 (1400 °C)	640	670	77.1

The results indicated that the higher carbonization temperature was beneficial to the oxidation resistance of the woodceramics. As shown in **Table 3**, when the samples were burned in air till 700 °C, the residues left increased greatly with the growth of carbonization temperature. Moreover, at the first stage, samples carbonized under 800 °C, 1000 °C, and 1400 °C exhibited a linear relation with its 9 % weight loss, being reached at 400 °C, 565 °C, and 640 °C, respectively. After a short period of accelerated weight loss, the remains of all samples decreased linearly until the end of the test. An exothermic peak and a small endothermic peak were observed between 400 °C and 500 °C, whereas these peaks disappeared on the other curves.

The weight loss of woodceramics was due to the reaction of carbon with O_2 . The TG-DSC results demonstrated that the carbonization temperature was a vital factor that affected the oxidation resistance of wood-



Figure 4: Effect of carbonization temperature on oxidation resistance of woodceramics (Weight ratio of wood to PF was 40:60; Heating rate of TG was 10 °C/min; Carbonization temperatures were (800, 1000, and 1400) °C; Gas environment of TG was Air)

ceramics. With the growth of the carbonization temperature, the starting thermal degradation temperature of woodceramics in air was extended into a higher temperature zone and its oxidation resistance was enhanced. It is well known that the oxidation resistance of woodceramics depends on its reactivity with O2. Based on previous studies involving the oxidation resistance of carbon materials,^{22,23} the oxidation deterioration of woodceramics under high temperatures experiences at least two steps: (1) oxygen diffusing through pores and cracks in the woodceramics to form surface oxides on the carbon surface; (2) reaction between carbon and oxygen to form CO₂, CO, and surface oxygen complexes. Further, it can be assumed that the oxidation resistance of woodceramics is affected by its microstructure, the portions of the surface which are active to react with O_2 (also known as active sites), and the reactivity of these active sites. The XRD results in this study illustrated the graphite-like, crystalline amorphous carbon structure of woodceramics, which was consistent with the research conducted by Qian et al.⁶ Nonetheless, the higher carbonization temperature contributed higher regularity of carbon.^{20,21} Although woodceramics inherited the hierarchical porous structure of wood powder, providing abundant oxygen pathways for carbon contacts,⁵ the higher carbonization temperature led to the increase of carbon content and crystallinity, and reduced the internal defects as well as heteroatoms of the woodceramics. Additionally, the carbon crystallization or crystallite growth would abate the reactivity of carbon materials.²⁴ Therefore, the oxidation resistance of the woodceramics was improved by increased carbonization temperature.

3.3 Component ratio vs. oxidation resistance

Figure 5 shows that, with the increase of PF content, the weight loss of woodceramics (carbonized under

800 °C) increased slightly. For all samples, the temperature inflection point of weight loss was in the range from 400 °C to 420 °C. At the temperature inflection point, the sample prepared with the highest weight ratio of wood powder to PF resin exhibited the fastest weight loss among all the samples. At 700 °C, the remaining sample weights were 25.8 % (50:50), 22.8 % (40:60), and 7.6 % (30:70). The results showed that, with the increase of PF resin ratio, the oxidation resistance of woodceramics decreased slightly due to the uneven carbonization of PF in woodceramics under 800 °C. As shown in Table 2, the higher the ratio of PF resin in samples, the lower the carbon content and higher the amounts of heteroatoms were obtained. Therefore, the unstable structure of samples contributed more weight losses when they were heated in air at high temperatures. The results showed that the increase of PF resin ratio was unable to enhance the oxidation resistance of woodceramics when they were fabricated under 800 °C.



Figure 5: Effect of component ratio on oxidation resistance of woodceramics (Weight ratios of wood to PF are 40:60, 50:50 and 30:70; Heating rate of TG is 10 °C/min, carbonization temperature is 800 °C; Gas environment of TG is Air)



Figure 6: Effect of heating rate on oxidation resistance of woodceramics (weight ratio of wood to PF is 40:60; Heating rates of TG are (2, 5, 10 and 20) °C/min; Carbonization temperature is 800 °C; Gas environment of TG is Air)

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The DSC curves in **Figure 5** show that a distinct exothermic reaction was exhibited between 370 °C and 450 °C. With the increase of PF resin ratio, the curve peaks shifted to the higher temperature range and covered a larger area. This phenomenon showed that the increase of heat release with the rise of PF resin ratio. After that, a small endothermic peak was observed, then the woodceramics continued to have an exothermic reaction. Theoretically, the reaction of carbon and oxygen in air is an exothermic reaction. DSC curves proved that the exothermic reaction was the most important reaction in the thermal decomposition of woodceramics.

3.4 Heating rate vs. oxidation resistance

As shown in Figure 6, the heating rate has a significant effect on the thermal decomposition of woodceramics. Before the rapid degradation, all the samples at four heating rates had low weight losses. With the heating rates of (2, 5, 10, and 20) °C/min, the starting temperatures of the rapid thermal decompositions were at (350, 380, 410, and 450) °C, respectively. With the rise of heating rate, the starting temperature of rapid thermal decomposition moved to a higher temperature zone. When the heating rates were at 2 °C/min and 5 °C/min, the thermal decomposition temperatures were terminated at 490 °C and 570 °C. However, when the woodceramics were treated under heating rates of 10 °C/min and 20 °C/min, their remaining weights were 22.8 % and 50.4 % at 700 °C, respectively, indicating that the thermal decomposition was uncompleted.

The DSC curves in **Figure 6** show that the four heating rates of all woodceramics appeared in exothermic, endothermic, and exothermic reaction sequence. It was revealed that there were some active groups in the woodceramics incompletely degraded when they were prepared under 800 $^{\circ}$ C.

The results showed that the speed of weight loss of woodceramics was reduced with the increase of heating rate. The performances of woodceramic products were



Figure 7: Conversion ratio of woodceramics using different heating rates of TG

stable under 300 °C. Therefore, the woodceramics (carbonized under 800 °C, weight ratio of 40:60) are able to be used in air below 300 °C for a long period of time or be used under an instantaneous high-temperature environment.

3.5 Apparent activation energy of the thermal decomposition reaction

The activation energy of a chemical reaction can be used to characterize its reaction rate and analyze the reaction mechanism. Using Equation (1), the conversion ratios of samples (the weight ratio of wood to PF resin was 40:60, the carbonization temperature was 800 °C, and heating rates of TG was (2, 5, 10, and 20) °C/min respectively) at any given time/temperature are shown in **Figure 7**.

Figure 7 illustrates that at 700 °C, the final conversion ratios of woodceramics were 81.2 % (heating rate of 10 °C/min) and 52.2 % (heating rate of 20 °C/min). However, when the heating rates were 2 °C/min and 5 °C/min, the conversions ended at around 500 °C and 590 °C.

With the increase of the heating rate, the starting temperature of rapid thermal decomposition moved slightly toward higher-temperature zones. Meanwhile, the ending temperature of thermal decomposition increased. Furthermore, through the Equation (2) and (3), the apparent activation energy E value can be obtained by calculating the slope of straight lines as shown in **Figure 7**. The calculated apparent activation energy are shown in **Table 4**.

Table 4: Apparent activation energies of thermal oxidation of wood-ceramics using the Ozawa method 17

Weight loss (%)	Apparent activation energy, <i>E</i> (kJ/mol)	R^2	
20	55	0.98909	
30	47	0.98889	
40	43.5	0.99614	
50	40.7	0.99624	
60	40.1	0.98417	
70	38.4	0.98056	

From **Table 4** and **Figure 7**, it was found that the apparent activation energy decreased with the increase of the weight loss of woodceramics. The activation energy was relatively high at the initial phase of the reaction. As the reaction proceeded, the activation energy declined.

The higher activation energy at the initial stage denoted that it was difficult for some carbon molecules to overcome the activation energy barrier to complete oxidation reactions. In another word, more energy were consumed to complete the oxidazation reaction at first, which was consistent with the TG-DSC results.

It is noteworthy that once some carbon molecules can overcome the activation-energy barrier and complete the reaction, they would release energy. The released energy supported other carbon molecules to surpass the energy barrier and lead to a chain reaction.²⁵ Consequently, this phenomenon contributed the higher oxidation rate of woodceramics during the second stage. In theory, the heat released from the thermal decomposition reaction can promote the degradation process of woodceramics. Furthermore, with the development of thermal degradation and carbonic oxides emission, the volume of inaccessible pores would diminish, making it easier for oxygen to reach the interior surface of carbon and accelerate the oxidation of woodceramics.^{26,27}

4 CONCLUSIONS

Woodceramics demonstrated good antioxidant properties in this research. Taking the sample prepared under 800 °C as an example, due to eliminating moisture and small molecule substance, the thermal weight loss in air at 350 °C was merely 9 %.

The carbonization temperature was an important factor that affected the oxidation resistance of woodceramics. Proliferating the carbonization temperature made it possible to improve the oxidation resistance of the woodceramics. The results highlighted the potential of woodceramics being used as catalyst supports.

The effect of PF resin content on the oxidation resistance was not as apparent as the carbonization temperature. With the increase of PF resin ratio, the thermal weight loss of woodceramics increased, oxidation resistance decreased, and heat release of thermal decomposition increased. Therefore, an optimal ratio of PF resin should be considered if it is desired that the woodceramics can provide sufficient mechanical properties when being used as catalyst supports.

With the growth of TG heating rates, the starting temperature of rapid thermal decomposition increased and slightly shifted to higher temperature zones. Meanwhile, the ending temperatures of oxidation degradation increased.

As the oxidation mass loss increased, the apparent activation energy of woodceramics declined. At the initial stage of reaction, the apparent activation energy of thermo-oxidative decomposition was relatively high. As the reaction progressed, the heat released by decomposition processes played an important role in helping the continuous reaction.

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