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ORIGINAL ARTICLE

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Pyrolysis of medium density fiberboard impregnated with phenol–formaldehyde resin

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Abstract Woodceramics (WCS) are new porous carbon materials that have been shown to possess many excellent properties, but the chemical mechanism during pyrolysis has not been reported yet. In order to investigate this process, pyrolysis of medium density fiberboard (MDF) was analyzed by thermogravimetry coupled with Fourier transform infrared spectroscopy (TG-FTIR) in this study. The results showed that the pyrolysis consisted of three stages up to 700°C. The first stage of the pyrolysis occurred below 240.0°C and was mainly due to moisture evaporation. The second stage between 240.0° and 390.2°C accompanied the main mass loss. The maximum pyrolysis speed (mass loss) was about 3.79% per minute at 313.2°C. This was believed to coincide with the cleavage of ether bridges between the wood material and phenol–formaldehyde (PF) resin, and pyrolysis of carbohydrate. At higher temperature, the pyrolysis of PF resin and lignin was the main reason for the mass loss in the third stage. The microcosmic environments of both the MDF and PF resin in the MDF treated with PF resin were different from the untreated MDF and PF resin, so that the temperatures at which their pyrolysis occurred and the quantities of evolved gases were different. During the process of WCS preparation, the rate of temperature increase should be very slow before it reaches 700°C, especially at around 313.2°C, at which point violent pyrolysis occurs. Such temperature control should allow uniform sintering of the sample and should reduce flaws in the product.

Key words Medium density fiberboard · Phenol–formaldehyde resin · Woodceramics · Pyrolysis · TG-FTIR

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Introduction

Woodceramics (WCS) are new porous carbon materials and their practical use has been anticipated in many fields of the industrial world.[1–6] The material has been proved to possess many good properties such as thermal resistance, corrosion resistance, oxidation resistance, and good shielding ability against electromagnetic waves. Therefore, potential uses as functional materials include electromagnetic wave shielding materials, friction materials, heat-insulating materials, and structural materials.

WCS are obtained by sintering wood or woody material impregnated with phenol–formaldehyde (PF) resin without oxygen. During sintering, the temperature is increased at a very low rate and large volumes of gas were released.[1] What happened and how did it happen? Knowledge of the chemical mechanism during pyrolysis can provide much insight into mechanism of WCS production and may provide some means of improving WCS properties. However, so far there has been little study on this subject.

In this study, the chemical reactions during pyrolysis of wood material impregnated with PF resin to form WCS were analyzed by thermogravimetry coupled with Fourier transform infrared spectroscopy (TG-FTIR). In the TG experiment, the sample was pyrolyzed under nitrogen following the same conditions used for WCS sintering. The gases produced during pyrolysis were able to be detected by FTIR as the samples gradually lost mass and gases evolved with increasing temperature.

Experimental

Three samples were analyzed by TG-FTIR. The components of all samples are shown in Table 1. Sample 1 was untreated medium-density fiberboard (MDF). Its glue was urea–formaldehyde (UF) resin. Hardwood fiber, which had been mixed with UF resin, had been pressed at 10 MPa and 120°C, to give the MDF. Sample 2 was PF resin cured at 120°C. Sample 3 was the MDF treated with PF resin. First,

the MDF sample, which was 5 mm in width, was treated under vacuum at 1.5 kPa for 2 h; then 40% PF resin was added and the pressure was maintained at 2 MPa for 4 h to make the PF resin penetrate into the MDF sample. Finally, the sample was brought back to normal atmosphere, air-dried, and heated at 120°C to cure the PF resin. All samples were prepared by being comminuted to pieces with a size range of 0.12 mm to 0.18 mm in particle diameter.

Thermogravimetry was performed with the STA449C (Netzsch, Germany). MAGNA760 FTIR and TG-DSC-FTIR (Nicolet, USA) were used for the FTIR spectroscopy. The samples were analyzed by TG at a linear heating rate of 5°C min^{-1} under pure nitrogen with a flow rate of 50 $cm^3 min^{-1}$, and the initiation temperature was 25°C. The evolved gases were analyzed by FTIR on-line. The FTIR detector was heated to 200°C in order to inhibit gas condensation. The mass of samples was about 10 mg.

Results and discussion

The TG curves of all samples are shown in Fig. 1. Curve 1 was for sample 1, the MDF sample; curve 2 was for sample 2, PF resin; curve 3 was for sample 3, MDF and PF resin composite; and curve 4 was calculated by adding curve 1 and curve 2, based on their component ratio in the composite of sample 3. In sample 3, MDF comprised 68.1% and PF resin comprised 31.9% of the whole mass. At a given temperature, the residue of MDF was R_{MDF} (%) and the residue of PF resin was R_{PF} (%), such that:

$$\text{Residue of sample 4}\,(\%) = R_{MDF} \times 0.681 + R_{PF} \times 0.319 \qquad (1)$$

The derivative thermogravimetry (DTG) curves based on the TG curves of all samples are shown in Fig. 2. Their thermogravimetric analysis data are shown in table 2. From Fig. 1 and 2 and Table 2, many differences between curves 3 and 4 were identified. Specific analysis was done as follows.

Table 1. Components of all samples

Samples	Hardwood fiber (%)	UF resin (%)	PF resin (%)
1	89.3	10.7	0
2	0	0	100
3	60.8	7.3	31.9

UF, urea–formaldehyde; PF, phenol–formaldehyde

Pyrolysis of MDF

MDF is a kind of woody material and shows similar pyrolysis behavior to that of wood. Among the three components of wood, i.e., cellulose, hemicellulose, and lignin, hemicellu-

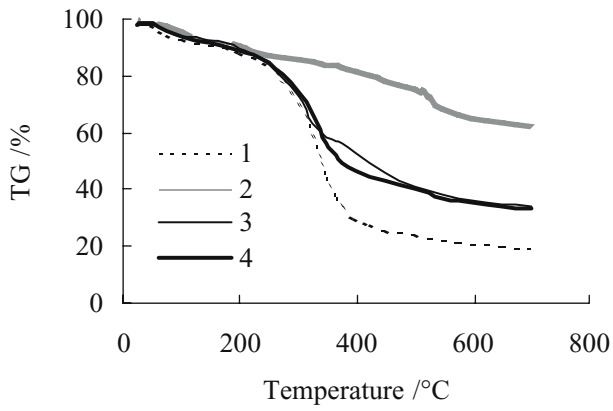

Fig. 1. Thermogravimetric (TG) curves of samples. Sample *1*, untreated medium-density fiberboard (MDF); sample *2*, phenol–formaldehyde (PF) resin cured at 120°C; sample *3*, MDF treated with PF resin; sample *4*, calculated curve obtained by adding the curves of samples 1 and 2 based on their component ratio in the composite of sample 3

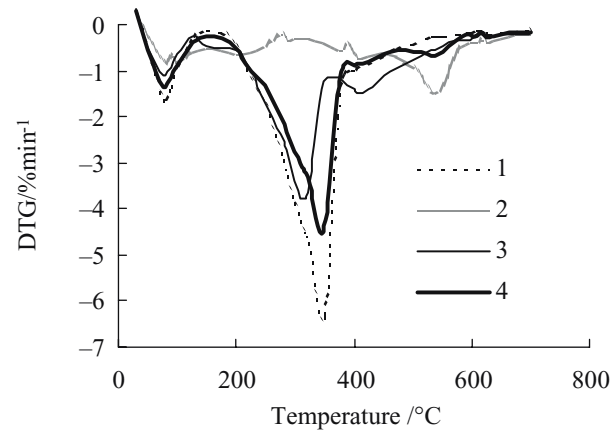

Fig. 2. Derivative thermogravimetry curves of samples (samples as defined in Fig. 1)

Table 2. Thermogravimetric analysis data under pure nitrogen

Samples[a]	Stage 1			Stage 2			Stage 3			Char residue %			
	$T_{initial}$ (°C)	R_{max} (% min^{-1})	T_{max} (°C)	$T_{initial}$ (°C)	R_{max} (% min^{-1})	T_{max} (°C)	$T_{initial}$ (°C)	R_{max} (% min^{-1})	T_{max} (°C)	400°C	500°C	600°C	700°C
1	25.0	1.63	73.6	213.0	6.15	349.7	382.2	–	–	30.1	24.0	21.0	19.2
2	25.0	0.84	80.1	260.9	1.50	537.2	560.8	–	–	82.0	75.4	65.5	62.7
3	25.0	1.12	74.6	240.0	3.79	313.2	390.2	1.47	406.0	52.5	40.9	36.1	34.0
4	25.0	1.38	77.0	213.0	4.45	349.7	382.2	0.88	400.0	46.7	40.4	35.2	33.1

$T_{initial}$, initial temperature of pyrolysis stage; R_{max}, maximum rate of mass loss; T_{max}, temperature at which R_{max} occurs
[a]Samples as defined in Fig. 1

Table 3. The assignment of Fourier transform infrared absorbance peaks

Group	Wavenumbers (cm^{-1})
Ar–OH (free)	~3610, ~1200
C–H (saturated)	2800–3000
C=C–H	3000–3100
N–H	~3400, ~927, ~963
O=C=O	~2350
C=O (carbon monoxide)	2109–2178
C=O (carbonyl)	~1730
Bezene ring	~1600, ~1580, ~1500, ~1450
Methane	~3000

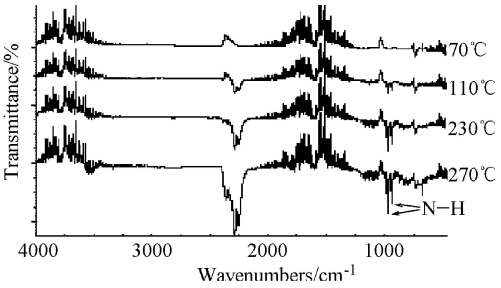

Fig. 3. Fourier transform infrared (FTIR) spectra of gas evolved from MDF pyrolysis in the first and second stages

lose is the most easily pyrolyzed.[7,8] Pyrolysis of hemicellulose starts at about 200°C and ends at about 400°C. The main pyrolysis stage of cellulose occurs from 300 to 400°C. Lignin continues pyrolyzing up to 700°C. Wood loses about 69.9% of its mass at 400°C and about 81.8% at 800°C. In the pyrolysis of both carbohydrates and lignin, H_2O, CO, CO_2, and CH_3OH are released. Methane (CH_4) is also given off during lignin pyrolysis.[7,9]

According to Fig. 1, pyrolysis of the MDF sample consisted of three stages. The first stage was between 25.0° and 213.0°C, a range in which the sample lost 9.84% of its mass, resulting mainly from moisture evaporation and partly from pyrolysis of hemicellulose and UF resin. The second stage was between 213.0° and 382.2°C. The mass loss in this stage was about 56.29% of the sample. The fastest rate of mass loss was about 6.3% per minute at 349.7°C. This was the main pyrolysis stage in which cellulose, hemicellulose, lignin, and UF resin were pyrolyzed. The third stage between 382.2° and 700.0°C was the last stage of the pyrolysis and only lignin continued to pyrolyze. The speed of mass loss decreased gradually. When the temperature reached 700.0°C, the mass was almost constant. The final mass of the pyrolyzed sample was about 19.2% of its initial mass.

In this experiment, MDF was a combination of wood fiber and UF resin. Therefore, besides the wood fiber, UF resin was also pyrolyzed during the MDF sample pyrolysis. The FTIR absorbance peaks of several groups are shown in Table 3.[10,11]

Figures 3 and 4 show the FTIR spectra of gas evolved from MDF pyrolysis at different temperatures. The absorption peaks of N–H and CO_2 originated from the UF resin and are very clear in the spectra. Ammonia (NH_3) and CO_2 were given off at 110°C and the gases evolved faster at 270°C. In the spectra for 400° to 650°C, the C–H absorption peaks were very small, indicating that very little low molecular weight hydrocarbon compounds was produced.

The gases that evolved from MDF pyrolysis were condensed and dried at low temperature, and then analyzed by FTIR. The results are shown in Fig. 5.

It can be seen in Fig. 5 that there was more organic acid in the vinegar liquid because O–H and C=O absorption peaks were more intense when compared with wood tar. The aromatic ring structure absorption of wood tar was stronger than that of vinegar liquid. Methylene (CH_2) absorption peaks of wood tar were also stronger than those of

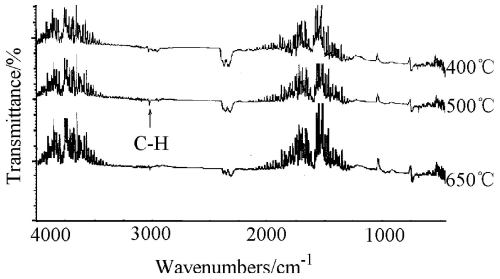

Fig. 4. FTIR spectra of gas evolved from MDF pyrolysis in the third stage

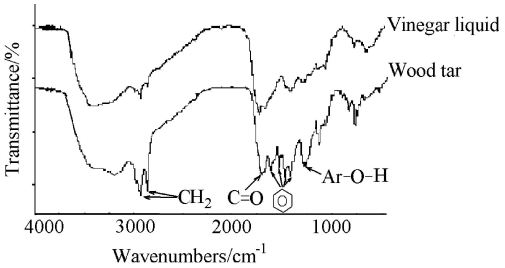

Fig. 5. FTIR spectra of condensed gas evolved from cellulose and lignin at room temperature

vinegar liquid because there were some long chain carboxylic acids in wood tar. However, these special absorption peaks were not clear, except for O–H absorption peaks, in the FTIR analysis of gas evolved from MDF pyrolysis because the concentrations of the components with these groups in evolved gas were too low to be detected by FTIR. In other words, the quantities of these components formed from MDF pyrolysis were small.

Pyrolysis of PF resin

It has been reported that the evolved volatile gases from PF resin pyrolysis are H_2O, phenol, cresol, CO_2, H_2, CH_4, CO, and C_2H_6.[12] Evolved phenol and cresol are identified as low molecular weight phenolic substances (LMS). According to TG and DTG curves of PF resin in Fig. 1 and 2, the pyrolysis of PF resin can also be divided into three stages. The first stage was between 25.0° and 260.9°C. The mass loss was

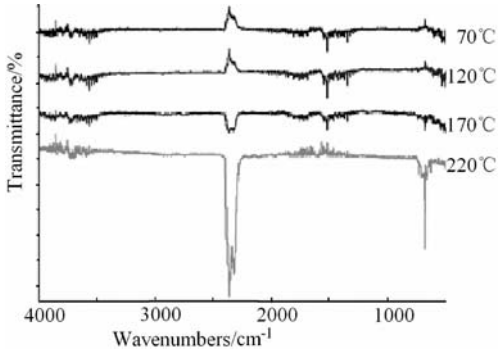

Fig. 6. FTIR spectra of gases evolved from PF resin pyrolysis in the first stage

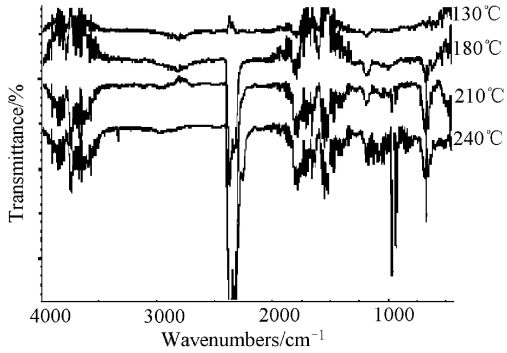

Fig. 8. FTIR spectra of gases evolved by pyrolysis of MDF treated with PF resin, first stage

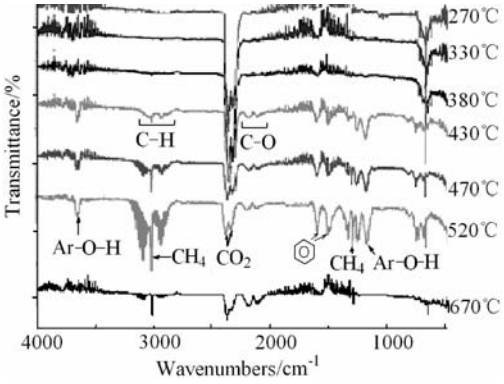

Fig. 7. FTIR spectra of gases evolved from PF resin pyrolysis in the second and third stages

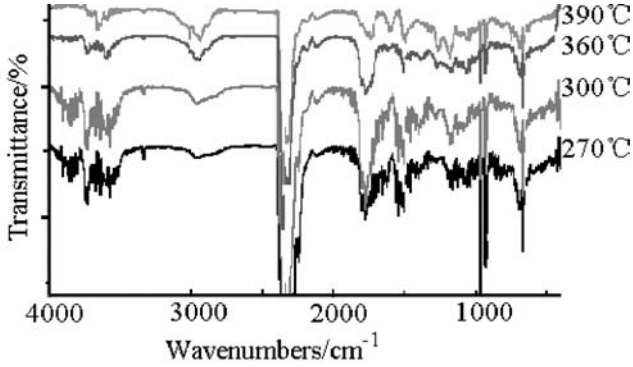

Fig. 9. FTIR spectra of gases evolved by pyrolysis of MDF treated with PF resin, second stage

12.64% in this stage and the speed of mass loss was about 0.5% per minute, resulting from the deep dehydration of solidified PF resin. The second stage between 260.9° and 560.8°C was the main stage of the PF resin pyrolysis and the mass loss was 19.57%. The fastest mass loss was 1.50% per minute and occurred at 537.2°C. Water, LMS, CO_2, CH_4, CO, and C_2H_6 were all evolved. The last stage of the PF resin pyrolysis was between 560.8° and 700.0°C. The mass loss speed was about 0.2% per minute at 700.0°C. The final mass of the PF resin was 62.6% of its initial mass. From the FTIR spectra of Figs. 6 and 7, H_2O, CH_4, C_2H_6, LMS, CO, and CO_2 were the main evolved gases.

Pyrolysis of MDF treated with PF resin

Similar to the pyrolysis of the MDF sample, the pyrolysis of MDF treated with PF resin consisted of three stages according to the TG result in Fig. 1. In the first stage between 25.0° and 240.0°C, the total mass loss was 13.6%. The maximum speed of mass loss was 1.3% per minute at 74.6°C. The mass loss of this stage was caused mainly by moisture evaporation and partly by pyrolysis of hemicellulose and UF resin. The H_2O, CO_2, and N–H absorption peaks are very clear in Fig. 8. In the second stage between 240.0° and 390.2°C, the mass loss was 32.5%. The maximum speed of mass loss was about 3.79% per minute at 313.2°C. This was the main stage of pyrolysis of cellulose and hemicellulose. The last stage was between 390.2° and 700.0°C. The total mass loss was 19.9% in this stage. The maximum speed of mass loss was about 1.47% per minute at 406.0°C, due mainly to pyrolysis of the PF resin. The rate of mass loss slowed gradually and the rate decreased to about 0.2% per minute at 700°C. The final mass was 34.0% of the initial mass.

The pyrolysis of MDF treated with PF resin was a very complicated process, although it was basically the combination of the pyrolysis of both the wood material and PF resin (Figs. 8–11). Carbon dioxide, H_2O, and NH_3 were released from the MDF, while H_2O, LMS, CO_2, CH_4, CO, and C_2H_6 were released from the PF resin. When the MDF treated with PF resin was pyrolyzed, the microcosmic environments of both MDF and PF resin were changed, resulting in changes in the pyrolysis mechanism, the temperatures at which their pyrolysis occurred, and the quantities of gases evolved. For example, CO_2 and NH_3 had been released at 110°C from the MDF sample, but not until 130°C for the MDF treated with PF resin. In the latter case, MDF was covered and filled in with PF resin, so that the release of CO_2 and NH_3 were postponed. The first stage of pyrolysis was much longer for the dehydration of PF resin condensation. In the second stage, the mass loss was much lower than that of the MDF pyrolysis because PF resin took up the

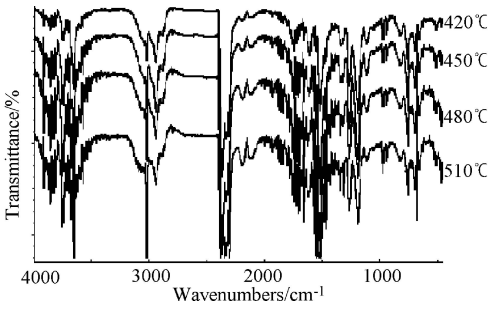

Fig. 10. FTIR spectra of gases evolved by pyrolysis of MDF treated with PF resin, first part of the third stage

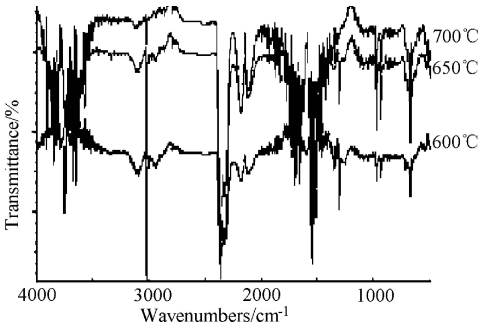

Fig. 11. FTIR spectra of gases evolved by pyrolysis of MDF treated with PF resin, second part of the third stage

31.9% of the sample mass and was not significantly pyrolyzed at that point. The MDF sample was pyrolyzed fastest at 349.7°C and the speed was about 6.15% per minute, but the maximum pyrolyzing speed of the MDF treated with PF resin was about 3.79% per minute at 313.2°C. It occurred earlier and appeared weaker than expected. Carbon monoxide was released at 300°C for the MDF treated with PF resin but was not evolved until the temperature reached 430°C for the PF resin. This result was attributed to the breaking of ether bridges and formation of CO as shown in Eq. 2–7.

$$\text{Wood–OH} + \text{HO–CH}_2\text{–Ar} \rightarrow \text{Wood–O–CH}_2\text{–Ar} + \text{H}_2\text{O} \quad (2)$$

$$\text{Wood–O–CH}_2\text{–Ar} \rightarrow \text{Wood–H} + \text{H–Ar} + \text{CO} \quad (3)$$

$$\text{Wood–O–CH}_2\text{–Ar} \rightarrow \text{Wood–Ar} + \text{CO} + \text{H}_2 \quad (4)$$

$$\text{Wood–OH} + \text{H–Ar} \rightarrow \text{Wood–O–Ar} + \text{H}_2 \quad (5)$$

$$\text{Wood–O–Ar} \rightarrow \text{O}^* + \text{Wood–Ar} \quad (6)$$

$$\text{O}^* + \text{C} \rightarrow \text{CO} \quad (7)$$

When PF resin penetrated into MDF and was heated to care, many hydroxyl groups of the wood material reacted with PF resin to form C–O–Ar or C–O–C ether bridges. During the pyrolysis, the ether bridges were easily broken to produce CO at about 300°C, and causing the maximum pyrolyzing speed to occur earlier than would be otherwise expected.

In the last stage from 390.2° to 700.0°C, the maximum speed of PF resin mass loss should occur at 537.2°C and large volumes of CH_4 and LMS were evolved from it. However, the maximum speed of mass loss occurred at about 406.0°C, much earlier than that of the PF resin, due to the pyrolysis of PF resin and lignin, and the main product gases were CO_2 and LMS. Methane was still evolved in the temperature range of 500–650°C. The reason might be that the linkage between PF resin and MDF is weaker than that in the PF resin itself.

It has been reported that WCS sintered at different temperatures below 700°C were very different in their properties and that the rate of temperature change affected on the quality of WCS.[1] This work further indicated that the chemical reactions occurred continuously below 700°C and the yield and properties of the products were changed during the WCS sintering process. The most violent pyrolysis occurred at 313.2°C, and was due mainly to MDF pyrolysis. When the temperture reached 700°C, gases were hardly generated and the chemical reactions were almost finished. Therefore, the rate of temperature increase rate must be very slow before it reaches 700°C, especially near 313.2°C, in order to sinter the sample uniformly and to reduce flaws in the products. The pyrolysis properties of the product WCS tended to be stable above 700°C.

Conclusions

The pyrolysis of MDF treated with PF resin could be divided into three stages. The first stage of the pyrolysis occurred before 240.0°C and was due mainly to moisture evaporation. The second stage between 240.0° and 390.2°C produced the main mass loss of 32.5%. The maximum pyrolysis speed was about 3.79% per minute at 313.2°C. This was the main stage of pyrolysis of cellulose and hemicellulose, and it occurred earlier and weaker than for MDF. This result was attributed mainly to the breaking of ether bridges breaking, which had formed between the wood material and PF resin, and to carbohydrate pyrolysis. At higher temperature, the pyrolysis of PF resin and lignin was the main cause of mass loss.

The microcosmic environments of both MDF and PF resin in the MDF treated with PF resin were different from the untreated MDF or the PF resin, so that the pyrolysis mechanism, the temperatures at which their pyrolysis occurred, and the quantities of gases evolved were different from those of untreated MDF or PF resin. For preparation of WCS, the rate of temperature increase rate should be very slow before it reaches 700°C, in order to sinter the sample uniformly and to reduce flaws in the products. When the temperature reached 700°C, gases were hardly generated and the chemical reactions were almost finished. The pyrolysis properties of the product WCS tended to be stable.

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