

Simulation on Pyrolysis Products of Thermoset Phenolic Resin with Different Chemical Structure and Experimental Validation

Honglin Hu¹, Lu Zhang², Liang Liu¹, Liqin Jiang¹, Na Huang¹, Zhiyu Chen¹, Ruilian Yu¹ and Zhizhong Meng³

1. Science and Technology on Advanced Functional Composites Laboratory, Aerospace Research Institute of Materials and Processing Technology, Beijing 100076, China

2. Science and Technology on Space Physics Laboratory, Beijing 100076, China

3. South China University of Technology, Guangzhou 510006, China

Abstract: The simulation on pyrolysis products of pure PF resin with different chemical structure was investigated and validated by pyrolysis gas-chromatography mass spectrometry (Py-GC/MS). The simulation of pyrolysis products of phenolic resin with different chemical structure was investigated by AMBER (Assisted Model Building with Energy Refinement) force field. The content of pyrolysis products phenol and cresol decreases with the increase of F/P (formaldehyde/phenol) value. The content of pyrolysis products dimethylphenol and trimethylphenol increases with the enhancement of F/P value. The crosslink density of phenolic mixture can be measured by the content of pyrolysis products dimethylphenol and trimethylphenol. Consequently, the results of simulation were validated by the Py-GC/MS experiment.

Key words: Simulation, pyrolysis products, phenolic resin, crosslink density.

1. Introduction

Advanced composites have been applied in the rigorous environments including high temperature and corrosion with the rapid development of technologies such as aerospace, military industry and so on. Therefore, more strict performance is urgently required for the composites. Polymer-based composites represent a excellent paradigm, which are widely used in rigorous environments. Their applications in high temperature fields are owing to the outstanding thermophysical property of carbon residue derived from the pyrolysis of organic resins. In the past decades, polymer matrix including phenolic resin [1], polyarylacetylene resin [2], and so on, was successfully used in the ablation composites

of the rocket and carbon/carbon composite.

Phenolic resin is the most widespread thermosetting resin of ablation composites [3], which possesses outstanding properties such as the resistances of heat, corrosion, wear, mechanics, adhesive capacity, etc. However, similar with other polymer-based composites, phenolic resin was also restricted due to the thermal degradation and failure. The disintegration of phenolic matrix resulting from pyrolysis destroys the basic structure of composites [4], which results in the failure of function composites. Therefore, it is an important issue for comprehending the mechanism and process of pyrolysis of phenolic resin. In order to understand the pyrolysis process of phenolic resin, many attempts aiming at theoretical [5] and experimental [6-8] methods were carried out. The pyrolysis mechanism of novolac phenol-formaldehyde resin cured by hexamethylenetetramine was reported in the literature [9].

Corresponding author: Honglin Hu, associate professor, research fields: polymeric composites, smart materials, phenolic resin.

To our knowledge, the research concerning the simulation of pyrolysis products of thermoset phenolic resin with different chemical structure has not been reported yet. In this paper, the simulation on pyrolysis products of pure PF resin with different chemical structure was investigated and validated by pyrolysis gas-chromatography mass spectrometry (Py-GC/MS).

2. Materials and Methods

2.1 Simulation Method

The first step involved drawing of the molecule's structural formula (Fig. 1). The AMBER (Assisted Model Building with Energy Refinement) force field of molecular dynamics was chosen to perform a molecular mechanics optimization. Finally, the

optimization configuration of molecule with lowest total energy was obtained. The final molecule size and periodic box size for simulation were listed in Table 1.

Next, pyrolysis process of phenolic resin with different chemical structure was simulated by AMBER force field, which only considered the bond breaking. The pyrolysis temperature of simulation starts from the initial 293 K to the final 1,173 K. Under the condition of vacuum, the heating time is 10 ps, the simulation time is 1 ps, and the time step is 0.001 ps. The total energy (E) and temperature (T) parameters are collected once per time step.

2.2 Materials

Phenol (P) and formaldehyde (F) were purchased

Table 1 Molecular size and periodic box size after optimization.

F:P	Molecular size	Periodic box size
1.0:1	10.304(Å)×5.475(Å)×13.610(Å)	20(Å)×10(Å)×20(Å)
1.2:1	10.582(Å)×7.510(Å)×13.075(Å)	20(Å)×15(Å)×20(Å)
1.4:1	10.199(Å)×6.166(Å)×15.182(Å)	20(Å)×10(Å)×20(Å)
1.5:1	10.590(Å)×6.687(Å)×13.799(Å)	20(Å)×10(Å)×20(Å)

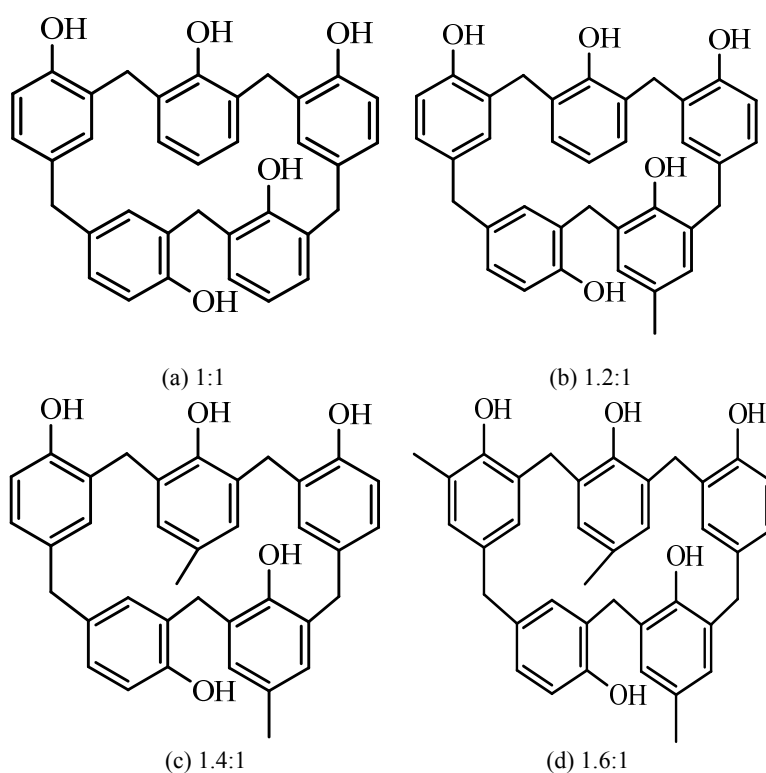


Fig. 1 Simplified model of phenolic resin for simulation.

from Sinopharm Chemical Reagent Co. Ltd. $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ used as a catalyst was purchased from Sinopharm Chemical Reagent Co., Ltd. Phosphoric acid was obtained from Tianjin Chemical Plant, China.

2.3 Synthesis of Phenolic Resin

F and P were mixed in a 250 mL three-neck round-bottomed flask with mechanical stirring at 40 °C. The mole ratio between F and P was 1.0:1, 1.2:1, 1.4:1, 1.6:1. Then $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ was added in the mixture under the agitation. Subsequently, the temperature of system raised to 60 °C and kept for 2 h, and 90 °C and kept for 1 h. And 10wt% phosphoric acid solution was added to the mixture for neutralizing the $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. The phenolic resin was obtained after vacuum dewatering and filter.

2.4 Characterization

Pyrolysis gas-chromatography–mass-spectrometry (PY-GC/MS) system was employed to separate and identify the pyrolysis volatiles. A PY-2020S (Frontier, Japan) pyrolyzer joining with GCMS-QP2010 (Shimadzu Co., Japan) mass spectrometer was used. The pyrolysis temperatures of 450 °C were used. The temperature of pyrolysis chamber before heating and during the separation of the volatiles was maintained at 200 °C. The separation of the volatile products was performed in a 30 m capillary quartz column. Before the chromatograph separation, the temperature of the chromatographic column was progressively increased as follows: (a) 40 °C for 3 min; (b) from 40 to 260 °C at a rate of 10 °C/min; (c) the capillary column was maintained at 260 °C for 10 min. Helium gas was used as the carrier gas. The mass range used for the mass selective detector was 19-500 m/z. The decomposition products were identified by means of the comparison between the experimental mass spectrum and the mass spectrum library attached to the PY-GC/MS apparatus. The identification of each volatile product can be confirmed if the qualification percentage reaches 85%

and even higher.

3. Results and Discussion

3.1 Simulation

Fig. 2 shows the simulation results of phenolic resin with different F/P value. The total energy and temperature parameters changing with simulation time is shown as Fig. 3. As the increase of simulation temperature, the bond breaks, releasing phenol, CH_4 , cresol, dimethylphenol and trimethylphenol. It is worth noting that the molecule number of phenol and cresol decreases with the rise of F/P value at temperature 1,173 K. At the same time, the molecule numbers of CH_4 , dimethylphenol and trimethylphenol increase. It infers that the content of phenol and cresol tends to reduce as the increase of F/P value, the content of CH_4 , dimethylphenol and trimethylphenol increases with the increase of F/P value. For the key reason, crosslink density of phenolic resin enhances with the raise of F/P value. Theoretically, the methylene of phenolic resin structure is formed from formaldehyde via addition and polycondensation reaction, which is acting as a connecting structure among phenols. As a result, phenol decomposes firstly from the structure under the condition of lower F/P, the content of dimethylphenol and trimethylphenol increasing with the enhance of crosslink density.

3.2 Experimental Validation

In order to prove simulation results, phenolic resins with different F/P value were synthesized. The concentrations of pyrolysis volatile products were analyzed by Py-GC/MS. Fig. 1 shows the total ion chromatograms of volatile products of phenolic resin with different chemical structure in the Py-GC/MS experiment at the temperature 723 K. The constituent identification of each peak is listed in Table 2.

As shown in Fig. 4, strong peaks of phenol and its methyl derivatives such as cresol and dimethylphenol are the main characteristic peaks for all resins, which

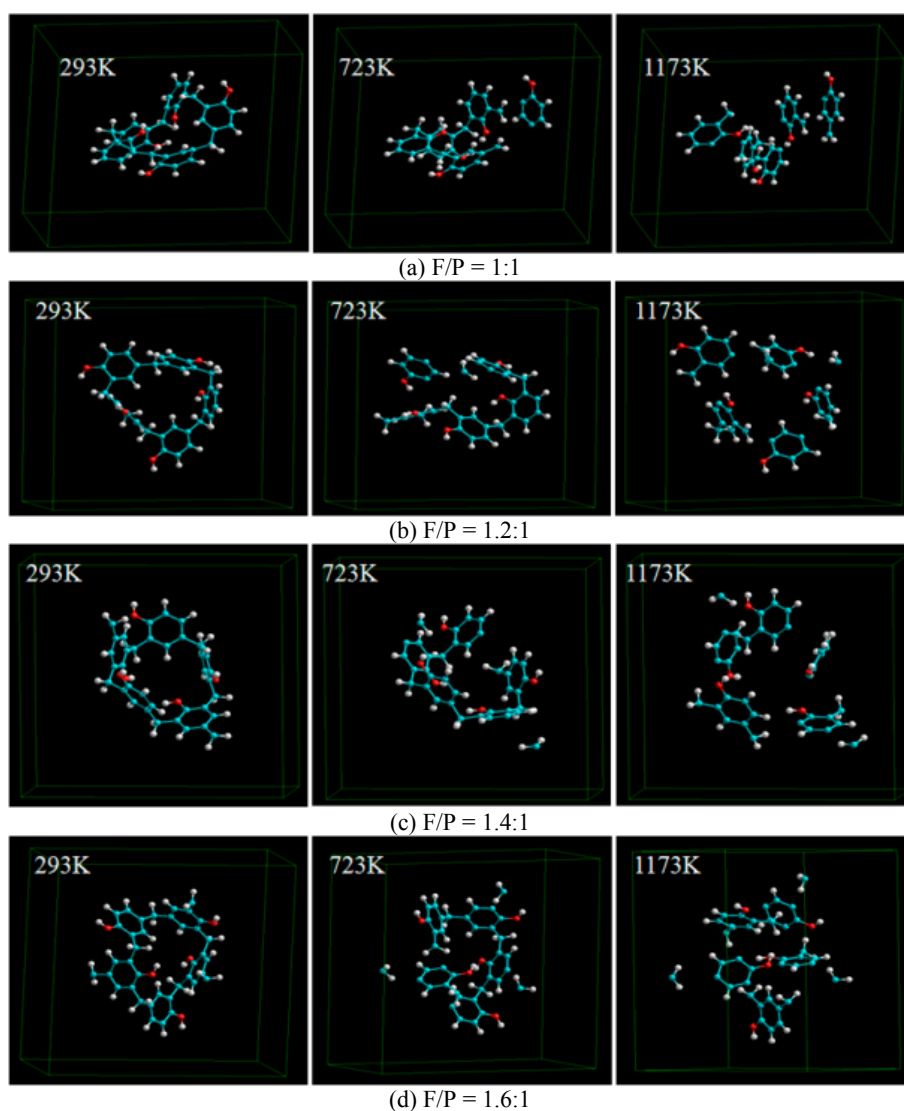


Fig. 2 The simulation results of phenolic resin with different chemical structure at temperature of 293 K, 723 K, 1,173 K.

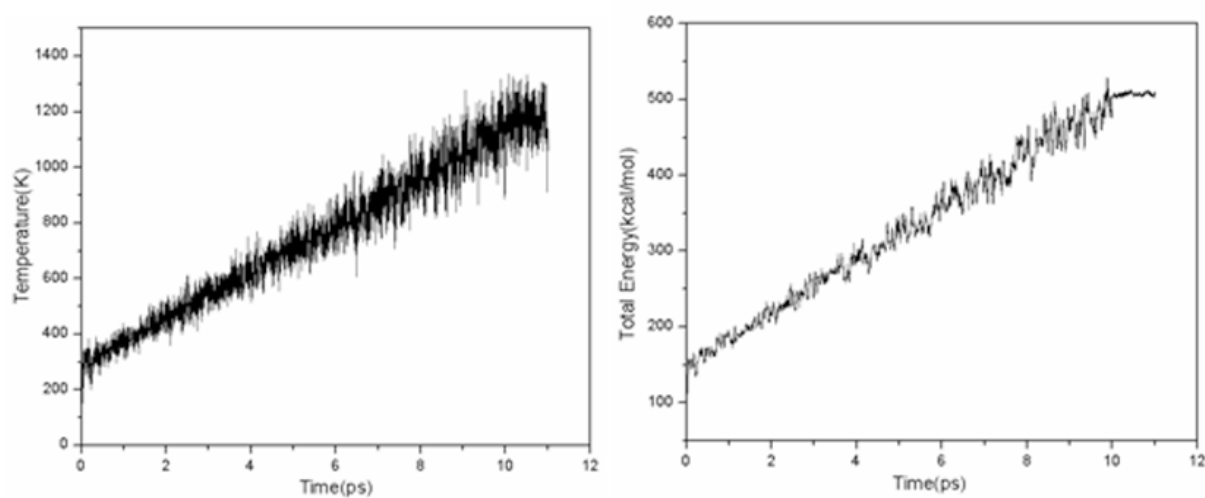


Fig. 3 The curve of total energy and temperature parameters with simulation time.

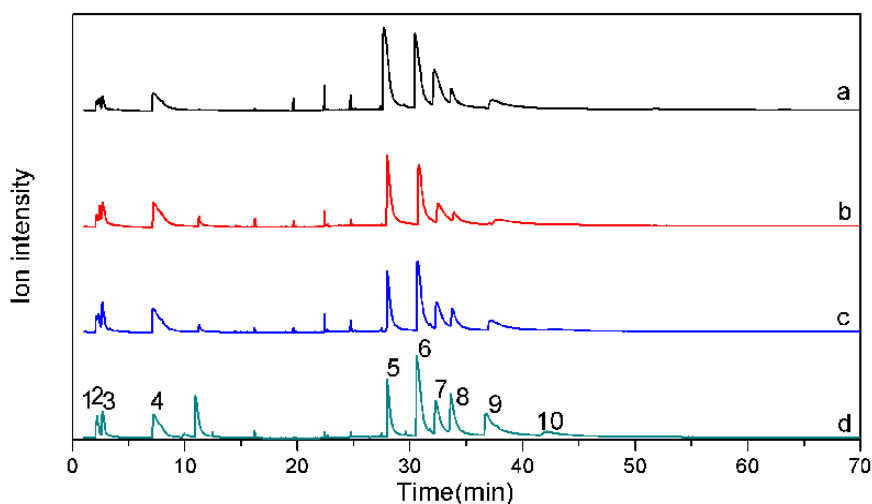


Fig. 4 Total ion chromatograms of volatile products of phenolic resin with different chemical structure at 723K. F/P value: a: 1.0; b: 1.2; c: 1.4; d: 1.6.

Table 2 Pyrolysis products of Py-GC/MS at 723 K.

Peak No.	Pyrolysis products	Peak area of ion intensity of ($\times 10^{-8}/\text{mg}$)			
		F/P = 1.0	F/P = 1.2	F/P = 1.4	F/P = 1.6
1	CO	0.365	0.363	0.352	0.325
2	CH ₄	0	0	0.771	0.948
3	CO ₂	1.014	1.205	1.339	1.474
4	H ₂ O	3.231	3.061	3.324	3.102
5	Phenol	15.065	7.475	4.732	3.652
6	O-cresol	11.525	5.415	4.531	4.019
7	P-cresol	8.112	2.301	2.534	2.791
8	2,6-dimethylphenol	2.28	2.321	2.312	3.193
9	2,4-dimethylphenol	2.191	2.124	2.413	2.515
10	2,4,6-trimethylphenol	0	0	0.235	0.842

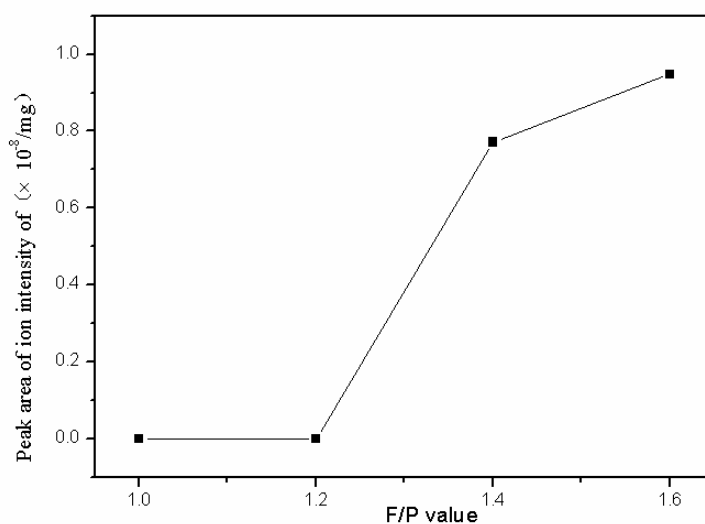


Fig. 5 The effect of F/P value on the content of pyrolysis product CH₄.

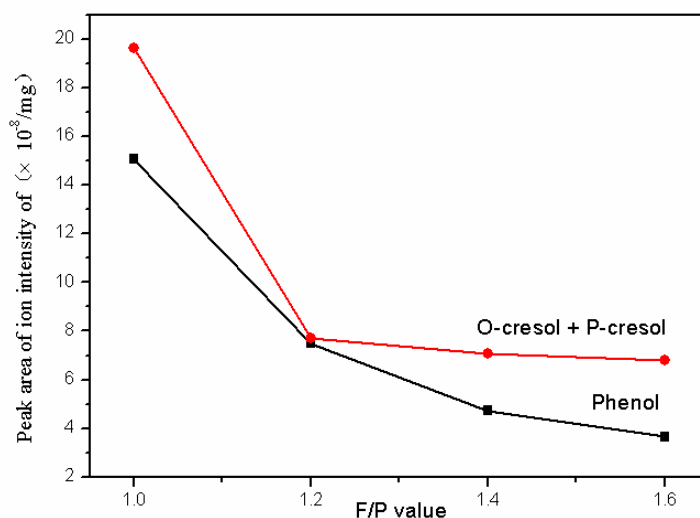


Fig. 6 The effect of F/P value on the content of pyrolysis products phenol and cresol.

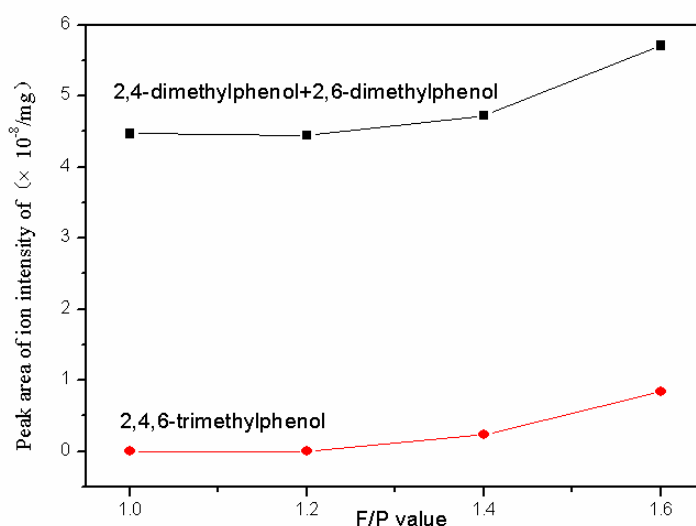


Fig. 7 The effect of F/P value on the content of pyrolysis products dimethylphenol and trimethylphenol.

is consistent with the simulation results.

The effect of F/P value on the content of pyrolysis product CH_4 is shown in Fig. 5. As the increase of F/P, the content of CH_4 raises, which is due to the rising content of methylene resulted from formaldehyde.

Fig. 6 shows the effect of F/P value on the content of pyrolysis phenol and cresol. The concentration of both pyrolysis phenol and cresol reducing with F/P value is obviously observed. The reason is that, crosslink density of phenolic resin decreases with the

decline of F/P, which results from the reduce of methylene acting as a connecting structure.

The effect of F/P value on the content of pyrolysis products dimethylphenol and trimethylphenol is shown in Fig. 7. Obviously, the content of both dimethylphenol and trimethylphenol increases with the enhancement of F/P, which infers that the crosslink density of phenolic resin enhances with the F/P. It also provides a strategy to measure crosslink density of phenolic mixture. As a result, the results of

simulation were validated by analysis of volatile products.

4. Conclusions

The simulation of pyrolysis products of phenolic resin with different chemical structure was investigated by AMBER force field. The content of pyrolysis products phenol and cresol decreases with the increase of F/P value. The content of pyrolysis products dimethylphenol and trimethylphenol increases with the enhancement of F/P value. The crosslink density of phenolic mixture can be measured by the content of pyrolysis products dimethylphenol and trimethylphenol. As a result, the results of simulation were validated by the Py-GC/MS experiment.

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