



Behavior investigation of phenolic hydroxyl groups during the pyrolysis of cured phenolic resin via molecular dynamics simulation



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ABSTRACT

In this paper, the initial stage of the pyrolysis process of phenolic resin has been simulated by ReaxFF (reactive force field) molecular dynamics simulation under various temperatures (3000 K, 3250 K, and 3500 K), to study the behavior of phenolic hydroxyl groups and to investigate the correlation between the production of small oxygen-containing molecules (including H₂O, CO and CO₂) and the quantity of hydroxyl radicals at different temperatures. We observed that the highly active phenolic hydroxyl groups would be easily turned into phenoxy radicals and hydroxyl radicals in primary evolution. And also, both the phenoxy radicals and hydroxyl radicals had remarkable impact on the following process of pyrolysis in secondary evolution: the formation of phenoxy radicals reduced the stability of the benzene ring and damaged backbone of phenolic resin accompanying with the release of CO molecules, while the hydroxyl radicals increased the amount of CO molecules and converted them into CO₂ molecules, to reduce the char yield of resin. We found that the amounts of small oxygen-containing molecules increased with the rise in the number of phenolic hydroxyl groups or the rise in the temperature. We also found that both the two evolution modes of phenolic hydroxyl groups (I. phenolic hydroxyl groups – phenoxy radicals – small oxygen-containing molecules; II. phenolic hydroxyl groups – hydroxyl radicals – small oxygen-containing molecules) can reduce the thermal stability of the backbone of resin. The negative effect of phenolic hydroxyl groups on the thermal stability of cured PR is valuable to the understanding of the pyrolytic process and char forming mechanism, and also the enhancement of the thermal stability of resin.

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1. Introduction

Investigation on the pyrolysis of phenolic resin (PR) is important for the application in the ablation resistance. It is well known that PR can be designed as the matrix of the composites substrates, to obtain materials with high heat capacity to absorb energy, or carry the thermal energy away by ablating themselves. One of the important applications is thermal protection systems which are required to shield spacecraft from the high temperatures generated in the stagnation region during atmospheric entry. The pyrolysis of PR is an extremely complicated physical and chemical process at high temperature which involves formation and quenching of various free radicals. To understand the pyrolysis of PR, the structure of PR network is a starting point: the basic structural unit

consists of three functional phenols and two functional methylenes [Fig. 1], and the main oxygen-carrying functional group is phenolic hydroxyl group. It has been proven by Ouchi and Trick from experiment that the oxygen-containing groups, especially the highly active phenolic hydroxyl groups, involved in the pyrolysis reaction first and turned into small oxygen-containing molecules which would take part in the reaction again [1,2].

However, it is difficult to explain the pyrolytic process and char forming mechanism because there is no consensus available on the way phenolic hydroxyl groups turning into small oxygen-containing molecules. It is hard to know the detail of pyrolysis by experimental method for the high temperature and the blistering reaction rate. Although some possible reaction mechanisms were proposed based on the experiment results, the generation of oxygen-containing molecules is still ambiguous. Trick et al. [2] put forward that some of H₂O molecules probably developed oxygen-containing radicals which would take part in reaction again by employing fourier transform infrared spectroscopy (FTIR) and gas

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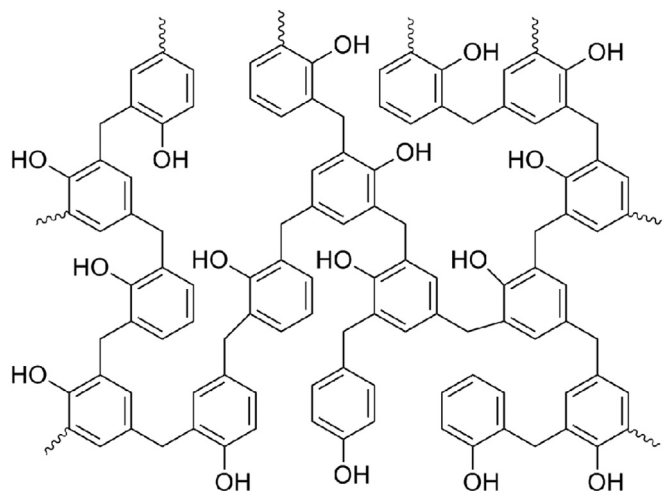


Fig. 1. Chemical structure of cured phenolic resin.

product evolution analysis. However, the formation mechanism for H₂O and other small oxygen-containing molecules, and the char forming mechanism still could not be elucidated. According to research of Jackson et al. [3] and Fitzer et al. [4] for cured phenolic resin with employing vapor-phase chromatographic methods and light and electron microscopy, oxygen elements involved in pyrolytic reaction through hydroxyl radicals. But the source of hydroxyl radicals could not be clarified, with the contradiction between the very little amount of hydroxyl radicals and the large quantities of small oxygen-containing molecules [5]. It has been found by Bauschlicher with Reactive force field (ReaxFF) molecular dynamics simulation for novolac that the O–H and C–O bonds with low energy in the phenolic hydroxyl groups, might participate in the reaction first and then initiate the following process [5]. Meanwhile, in our previous researches of modified boron-containing phenolic resins [6,7], it has been found that parts of the phenolic hydroxyl groups were blocked by the phenyl boronates generated from the reaction of phenolic hydroxyl groups and boric acid or phenyl boronic acid [Fig. 2], which reduced the reactions based on the phenolic hydroxyl groups and thus improved thermal stability of the resin. Therefore, we considered that the reactions based on the phenolic hydroxyl groups may be the reason for the low char yield and the low thermal decomposition temperature of PR. There may be several different evolution modes of phenolic hydroxyl groups, which lead to different ways of the damage to the resin backbone. This evoked our interest to study the pyrolysis process of

phenolic hydroxyl groups and get a new understanding about the pyrolytic process of cured PR.

Molecular simulation provides us a new possibility to further understanding of the thermal degradation of polymers. ReaxFF, which was used to describe the bond formation, breaking and reactivity, is a powerful method to study the course of pyrolytic process [8–10]. In recent years, this method has been successfully applied in the research of both high-*ortho* novolac and cured PR [11–13]. For example, ReaxFF was found to show enough accuracy to simulate the pyrolysis process of high-*ortho* novolac PR by Qi et al. [14]. And also, ReaxFF was performed by Jiang et al. [12] and Desai et al. [13], to simulate the pyrolysis of high-*ortho* novolac PR at the initial stage under various temperatures from 2000 K to 4000 K and they found that H₂O molecules were formed in three ways. However, the mechanism of the pyrolysis process of cured PR which has wide applications in ablation resistance, is still ambiguous. Till [11] investigated the early stage gas evolution during pyrolysis of both novolac PR and cured PR using ReaxFF molecular dynamics method and found that the kinetic parameters for the evolution of the single species, water, appeared to be strongly dependent on the cross-linking present in the structural mode. Considered the success of ReaxFF in novolac PR systems, using ReaxFF based on molecular dynamics in cured PR system to investigate the behavior of phenolic hydroxyl group in the pyrolytic process and the formation mechanism of small oxygen-containing molecules can be a good choice.

Based on above consideration, in this paper, we presented the simulation with ReaxFF of the initial stage of the pyrolysis process of cured PR under various temperatures (3000 K, 3250 K, and 3500 K). We observed that the oxygen element of the phenolic hydroxyl groups can transform to small oxygen-containing molecules (including H₂O, CO and CO₂) in two evolution modes (I. phenolic hydroxyl groups – phenoxy radicals – small oxygen-containing molecules; II. phenolic hydroxyl groups – hydroxyl radicals – small oxygen-containing molecules). And also, the amounts of small oxygen-containing molecules are increased with the rise in the number of phenolic hydroxyl groups or the rise in the temperature. We found that both the two evolution modes of phenolic hydroxyl groups in the pyrolysis process can lead to a great deal of damage to the backbone of resin. It is very useful in revealing intrinsic factors influencing the thermal stability of resin and designing resin materials with high performance in ablation resistance.

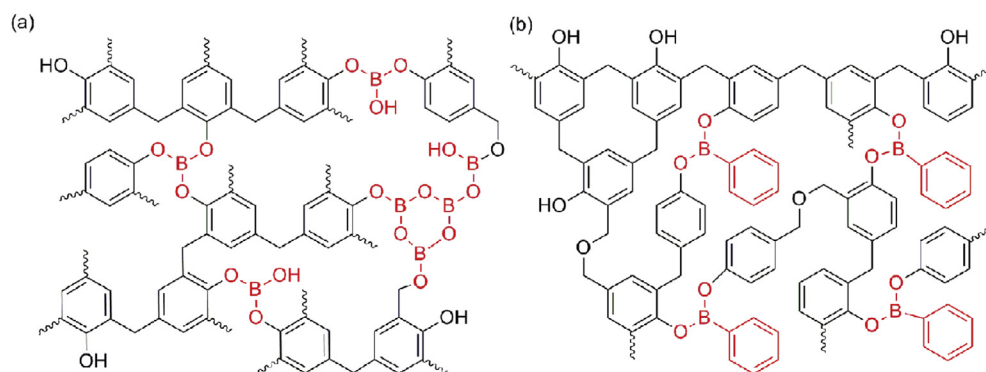


Fig. 2. Chemical structure of boron-containing phenolic resins. (a) Boron acid modified phenolic resin; (b) Phenylboronic acid modified phenolic resin. The structure of boronates were highlighted by red color. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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