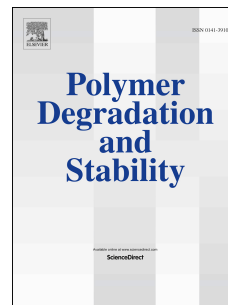# Accepted Manuscript

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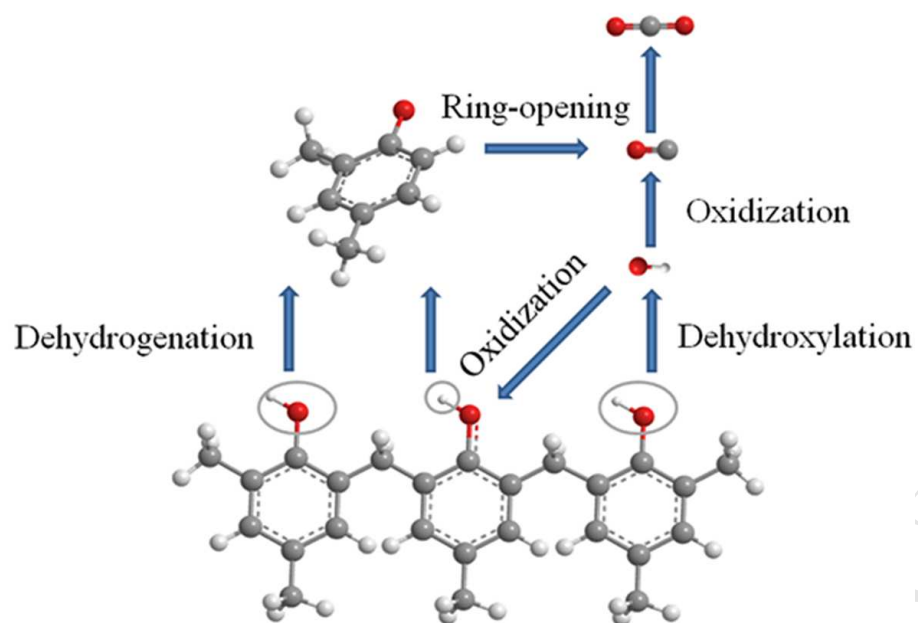
Behavior Investigation of Phenolic Hydroxyl Groups during the Pyrolysis of Cured Phenolic Resin via Molecular Dynamics Simulation

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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 investigate the correlation between the production of small oxygen-containing molecules (including H_2O, CO and CO_2) and the quantity of hydroxyl radicals at different temperatures. We observed that the highly active phenolic hydroxyl groups would be easily turned into phenoxyl

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radicals and hydroxyl radicals in primary evolution. And also, both the phenoxyl radicals and hydroxyl radicals had remarkable impact on the following process of pyrolysis in secondary evolution: the formation of phenoxyl 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 CO_2 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 - phenoxyl 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, which is valuable to the understanding of the pyrolytic process and char forming mechanism of resin.

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 can carry the thermal energy away by ablate 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 the 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

[Figure1], and the main oxygen-carrying functional group is phenolic hydroxyl group. It is accepted that at the beginning of the pyrolysis of PR, functional groups with low bond energy (such as phenolic hydroxyl group) participated in the homolytic reaction and produce some living radicals, which would initiate the following reaction with releasing some small molecule compounds. And also, it has been proven by Ouchi and Trick that the oxygen-containing groups, especially the highly active phenolic hydroxyl groups, involved in the reaction first and turned into small oxygen-containing molecules which would take part in the reaction again[1-2].
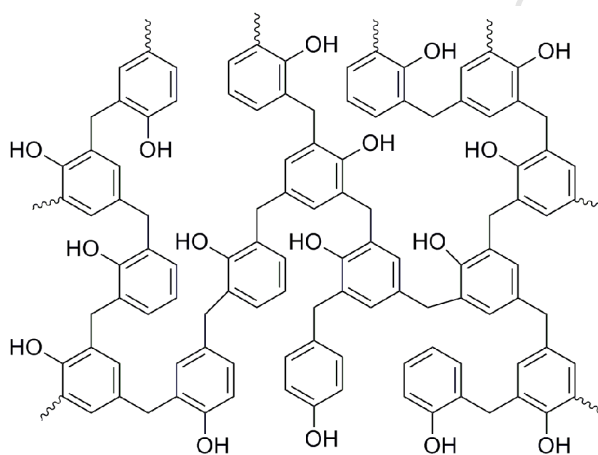

Figure 1. Chemical structure of cured phenolic resin.

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] considered that some of H_2O molecules probably developed oxygen-containing radicals which would take part in reaction again. However, the formation mechanism for H_2O and other small oxygen-containing molecules, and the char

forming mechanism still could not be elucidated. According to Jackson et al.[3] and Fitzer et al.[4], 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 using Reactive force field (ReaxFF) molecular dynamics simulation 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]. Therefore, we considered that the reaction based on the phenolic hydroxyl groups may be the reason for the low char yield and the low thermal decomposition temperature of PR. And also the different evolution modes of phenolic hydroxyl groups should 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 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[6-8]. In recent years, this method has been successfully applied in the research of high-*ortho* novolac PR[9-11]. For example, ReaxFF was found to show enough accuracy to simulate the pyrolysis process of high-*ortho* novolac PR by Qi et al. [12] And also, ReaxFF was performed by Jiang et al. [10] and Desai et al. [11], 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 H_2O 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 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, to investigate the behavior of phenolic hydroxyl group in the pyrolytic process of cured PR and the formation mechanism of small oxygen-containing molecules with ReaxFF based on molecular dynamics can be a good choice.

Based on above consideration, in this paper, we presented the simulation of the initial stage of the pyrolysis process of cured PR with ReaxFF under various temperatures (3000 K, 3250 K, and 3500 K). We observed that oxygen element of phenolic hydroxyl groups can transform to small oxygen-containing molecules (including H_2O, CO and CO_2) in two evolution modes (I. phenolic hydroxyl groups - phenoxyl 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 backbone of resin. It is very useful in revealing intrinsic factors influencing the thermal stability of resin.

2. Method

2. 1 Building the model

The experience of Izumi et al.[13] was used for reference. Parameters of models are listed in Tables 1, which obtained based on the proportion of Izumi's statistical results that came from the average value with 20 cross-linked structures. The structure model of cured PR was constructed with adopting molecular dynamics method which based on the DREIDING[14] force field. The

final cross-linked models of PR were obtained by cross-linking reactions of linear polymers under 3D boundary conditions. Detailed procedures are described in the following subsections.

2.1.1 Amorphous structure of uncross-linked polymers. The linear novolac-type PR was constructed as primary structure with the degree of polymerization being 5. Amorphous structures of uncross-linked phenolic resins were obtained by the following procedure: (i) in a cubic MD cell under the 3D periodic boundary condition, 12 polymers whose the degree of polymerization were chosen to be 5 and were in *ortho -ortho* configuration, were randomly placed and the size of the cell was adjusted to have the density (d) of 0.3g/cm^3. (ii) The polymers were stirred for 200 ps in the canonical (NVT) ensemble (T = 600 K and the integration time step of the velocity Verlet algorithm t= 1 fs). This high temperature (600 K) was chosen to generate more possible conformations effectively. The geometrical and topological independence of polymer structures generated at every 10 ps was confirmed through an evaluation of the pair-distribution function of carbon atoms of the methylene groups. (iii) Twenty instantaneous structures obtained every 10 ps during the stirring process were compressed in the isothermal–isobaric (NPT) ensemble (T = 450 K, the external pressure (P) =10 GPa, and t = 0.5 fs) to give structures with d equal to 1.5 g/cm^3. (iv) The compressed structures were relaxed in the NPT ensemble (T=450 K, P =0.1 MPa, and t =0.2 fs) to give 20 different amorphous structures of uncross-linked phenolic resins with d equal to 0.98 g/cm^3, which guarantees the density being in 1.25 after cross-linking reaction. The temperature of 450 K was chosen considering the typical molding and curing temperature in the manufacturing process. The Nose‐Hoover algorithm[15] was used for the temperature control, and the Andersen[16] was used for pressure control in isotropic cubic cells.

2.1.2 Cross-linking reaction. The cross-linking reactions, were performed as described in the following procedure: (v) a pair of reactive carbons at the first nearest neighbor and not on the same phenolic ring was chosen, in which the reactive carbons denote the hydrogen-substituted o- or p carbons that are adjacent to the hydroxyl group of a phenolic ring. (vi) Two hydrogens attached to the chosen carbons were removed. (vii) A methylene was inserted between the positions of these carbons from which the hydrogens had been removed. (viii) The carbons were connected via the carbon of the inserted methylene group. These procedures (v)–(viii) were repeated until the degrees of cross-linking (D) reached 0.75. Here D is defined by $D=(2N_{CH2})/(3N_{PhOH})$, where N_{CH2} and N_{PhOH} denote the number of methylene groups and phenolic rings in a unit cell, respectively. The partial charges were reassigned to the resulting new structures to give 20 different cross-linked structures.

2.1.3 optimizing the model. Optimization procedure includes relaxation and anneal and both of them were carried out in the NVT ensemble. Relaxation, which can eliminate the unreasonable structure in the process of building box, was made up of energy minimization and NVT molecular dynamics simulation. Then anneal was performed to further eliminate the unreasonable structures. After anneal, the model of cured PR with lowest energy was chosen for further calculation.
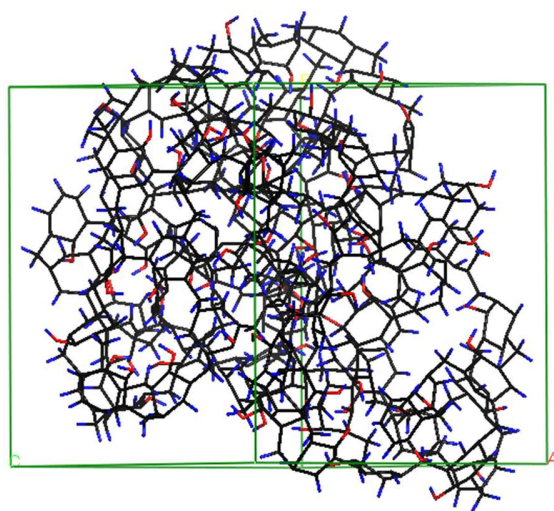
Figure 2. Snapshot of the he cured PR structure model.

Color code: C, black; O, red; H, blue.

Table 1: structure parameters of building the cured PR structure models

molecular formula	molecular weight/D	density/ g/cm^3	$n_{Ph\text{-}OH}$[a]	n_{CH2}	$n_{CH2(o\text{--}o)}$[b]	$n_{CH2(o\text{--}p')}$	$n_{CH2(p\text{--}p')}$
$C_{430}H_{382}O_{60}$	6502	1.25	60	68	45	8	17
$C_{430}H_{382}O_{50}$	6342	1.25	50	68	45	8	17
$C_{430}H_{382}O_{40}$	6182	1.25	40	68	45	8	17

a) n is the number of specific structure in cured model, subscript stands for the type of functional group. PhOH stands for phenol ring. CH_2 stands for methylene. CH_3 stands for methyl.

b) The *o–o'*, *o–p'*, and *p–p'* stand for the *ortho- ortho*, *ortho- para* and *para - para* sites in the different bridging modes of methylene to connect the benzene rings.

2.2 Simulation process

The parameter set of Chenoweth et al. [17], the ReaxFF program developed by van Duin et al[18] and the software, ADF(Amsterdam Density Functional), was used for our simulations. The Chenoweth parameter set was originally developed for hydrocarbon combustion. As in the original Chenoweth paper[13], an extra triple bond energy correction for stabilizing CO is also activated. The system is initially equilibrated at a constant temperature of 600 K and using a constant volume NVT canonical ensemble for 100 ps to equilibrate and then performed at 3000, 3250 and 3500 K for 20 ps to investigate pyrolysis reaction. A Berendsen thermostat[19] was employed along with a 0.25 fs time step. Structural models with the number of phenolic hydroxyl groups being 40, 50 and 60, respectively were constructed by eliminate phenolic hydroxyl groups from the model of curd PR randomly, and then the pyrolytic process was simulated under the same condition.

3. Results and discussions

3.1 Primary evolution of phenolic hydroxyl group

In cross-linked structure of cured PR, phenolic hydroxyl groups which constitute the high reactive sites involve in reaction first, producing the phenoxyl radicals and hydroxyl radicals with high reaction activity, and then generating small oxygen-containing molecules. As O-H bond and C-O bond with lower energy[5] (the values are 110.3 kcal/mol and 115.4 kcal/mol, respectively), some phenolic hydroxyl groups easily decompose to phenoxyl radicals and hydroxyl radicals at the initial stage of pyrolysis. With tracking the generation process of the small oxygen-containing molecules (Figure 3) in the simulated result of the model in which the number of phenolic hydroxyl groups is 60 (named NOH-60), we found that the phenoxyl radicals

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and hydroxyl radicals, as the key active intermediates, play decisive roles in the production of small oxygen-containing molecules following the order of H_2O, CO and CO_2. The order is consistent with that observed by Till et al.[9] in the research of thermal effect of the pyrolysis progress of cured PR by ReaxFF. Considering that the functional groups to produce H_2O should be the most active groups and H_2O molecules are produced by the condensation reaction of phenoxyl hydroxyl groups, the phenoxyl hydroxyl groups should exhibit the highest reactivity with comparing to other functional groups. The number of small oxygen-containing molecules was shown in Table 2. From the summary of the number of small molecules most of the phenolic hydroxyl groups were found to turn into small oxygen-containing molecules, confirming the high activity of the phenoxyl hydroxyl [20].

To investigate the influence of phenolic hydroxyl groups, other two models with fewer phenolic hydroxyl groups are generated by eliminating phenolic hydroxyl groups from the model of curd PR randomly. These models in which the number of phenolic hydroxyl groups is 50 and 40, are named NOH-50 and NOH-40, respectively. By simulations of these models at 3500 K, we found that the phenolic hydroxyl group exhibits high activity and plays an important role in pyrolysis process of PR. Statistic on the quantity of all products in the pyrolysis of NOH-60, NOH-50 and NOH-40 models (Figure 4) shows that the production is increased with rise in the number of the phenolic hydroxyl groups: the highest production is observed in the NOH-60 system which is rich in phenolic hydroxyl groups and the lowest production is observed in the NOH-40 system with the minimum of phenolic hydroxyl groups. This is also similar to Ouchi's research in the pyrolysis of novolac resin that [1] the more hydroxyl groups in the sample, the more products in the system. It is due to that the structure with more phenolic hydroxyl groups can produce more phenoxyl radicals and hydroxyl radicals, which promote the following reaction

and lead to more products. Thus, the phenolic hydroxyl group plays a vital role at the initial stage of pyrolysis and it is meaningful to trace the evolution of phenolic hydroxyl groups in detail. Nevertheless, other functional groups such as methylene would also take part in reaction and turn into products, which made the relationship between the numbers of the pyrolysis products and the phenolic hydroxyl groups in our simulation seems to be nonproportional.

Table 2: The number of small oxygen-containing molecules products in the simulation of structure models (NOH-60, NOH-50 and NOH-40 stand for the models in which the number of phenolic hydroxyl groups is 60, 50 and 40, respectively) after 20 ps simulation.

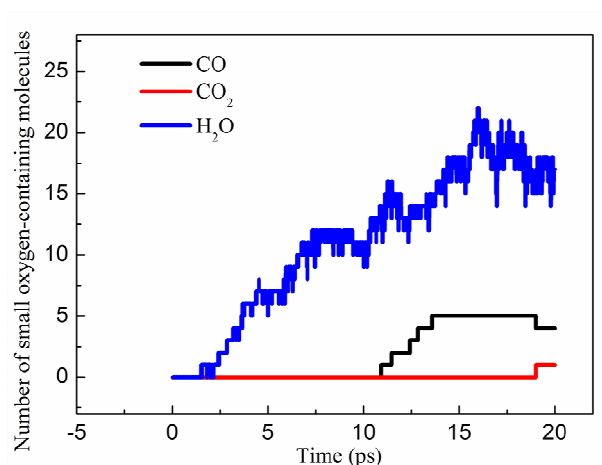| Model ID	No. of H_2O	No. of CO	No. of CO_2	Summation	Proportion/%
NOH-60	21	4	1	26	43.33
NOH-50	14	8	0	22	44.00
NOH-40	13	6	0	18	45.00

Figure 3. Distribution of the main small oxygen-containing molecules (including H_2O (blue),

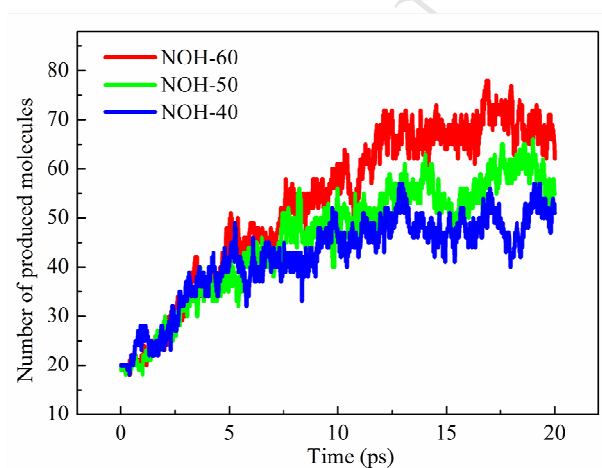CO (black) and CO_2 (red)) with time in the simulation of NOH-60 model at 3500 K.

Figure 4. Distribution of produced molecules with time in the simulation of NOH-60 (red),

NOH-50 (green) and NOH-40(blue) models with different numbers of phenolic hydroxyl groups

at 3500 K.

3. 2 Secondary evolution of phenolic hydroxyl group

3.2.1 Phenoxyl radical

Phenolic hydroxyl groups in PR converted into phenoxyl radicals and hydroxyl radicals in primary evolution. For phenoxyl radicals, there are two reactions involving in the transformation from radicals to CO molecules (Figure 5, reaction 1 and 2). In reaction 1, the first step is the loss of the hydrogen from the phenolic hydroxyl groups and then next series of steps shifts a C−C bond, thus the initial six-membered ring turns into a five-membered ring with the release of CO molecules. Reaction 2 starts by adding carbon radicals to phenoxyl radicals and then a series of molecular rearrangement reactions are observed during the next steps and finally the formation of CO molecules are identified. Both of reaction 1 and 2 would change the backbone of PR and reduce the char yield. The highly active phenoxyl radicals would involve into reaction in few femtoseconds and generate phenolic hydroxyl groups and CO molecules. Some of these phenolic hydroxyl groups may transform into phenoxyl radicals again so there are also a number of phenoxyl radicals maintained in the system. Analysis of ten events of CO formation from 3000 K to 3500 K shows that some CO molecules are generated through reaction 1 from phenoxyl radicals at the initial stage of PR carbonization, which is consistent with the mechanism of CO formation in novolac PR system proposed by Qi et al.[5] As the pyrolysis reaction going on, the benzene ring is opened and some carbon radicals are produced under high temperature, and CO molecules are produced both by reaction 1 and 2. Therefore, the dehydrogenation of the phenolic hydroxyl groups is crucial to the generation of CO molecules, which also lead to low char yield. This also can be confirmed by the high char yield of PR modified by boron, silicon or other elements[21-24]: the modifiers block parts of phenolic hydroxyl groups and reduce the number of phenoxyl radicals, finally result in the high char yield. A comparison between the distribution of phenoxyl radicals and CO with time may be helpful to verify above analysis, but we cannot obtain this for the complexity of distribution of phenoxyl radicals. In addition, there is no

consensus available on the source of CO molecules: all CO molecules are produced by ring-opening reaction from molecular simulation[5], while according to the traditional experimental studies CO molecules are generated by the oxidation of the methylene[4]. One of the possible reasons is the limited temperature conditions of experimental studies and this issue is still open to further study.
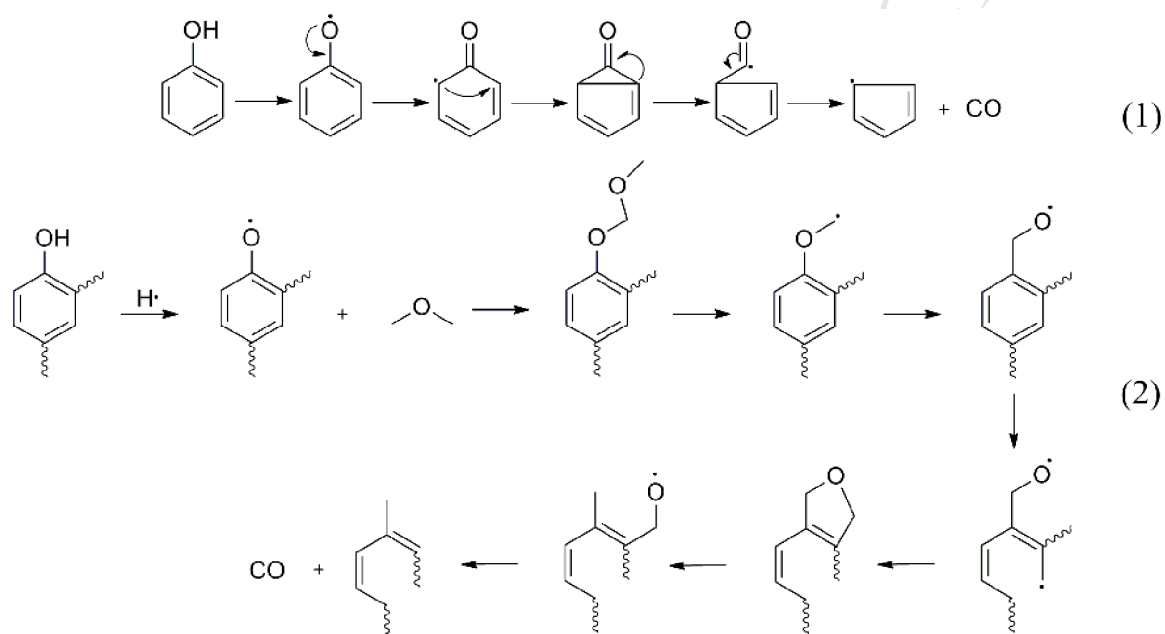

Figure 5. Mechanism of CO formation in the pyrolysis simulation of NOH-60 model at 3500 K.

On the other hand, there is an inhibiting effect to the formation of CO molecules from the phenoxyl radicals. CO should have been the main small oxygen-containing molecules because phenoxyl radical is the main component of the dehydrogenation reaction which is easy to happen, and phenoxyl radicals would evolve into CO gradually. However, according to statistics analysis (Table 2), the main small oxygen-containing products are H_2O molecules but not CO molecules (The number of H_2O is 21 while the number of CO is 4). The reason is that the phenolic

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hydroxyl groups obtained from the reaction between phenoxyl radicals and hydrogen free radicals may transform into hydroxyl radicals, which reduced the amount of phenoxyl radicals and then reduced the amount of CO molecules. From this viewpoint, this reaction (phenoxyl radicals and hydrogen free radicals) may lead to a side effect of slowing down the process of pyrolysis with reducing the amount of highly active free radicals.

3.2.2 Hydroxyl radical

As mentioned above, hydroxyl radicals with high oxidization are generated from the primary evolution of phenolic hydroxyl groups. In order to investigate the effects of hydroxyl radicals on pyrolysis reaction, we simulate the pyrolysis of NOH-60 model at 3000 K, 3250 K and 3500 K, respectively. As shown in Figure 6, the maximum production of hydroxyl radicals is observed at 3500 K. The fact that the number of hydroxyl radicals increased with the temperature increasing is consistent with the regulation pattern in the novolac PR system found by Qi et al.[12]. At 3500 K, a relative large number of hydroxyl radicals which can oxidize other functional groups strongly are produced (Figure 6), and it results in the increase of the number of small oxygen-containing molecules (including CO, CO_2 and H_2O) and the decrease of the char yield. We'll go into further detail about the formation mechanism of the CO, CO_2 and H_2O molecules from hydroxyl radicals below.
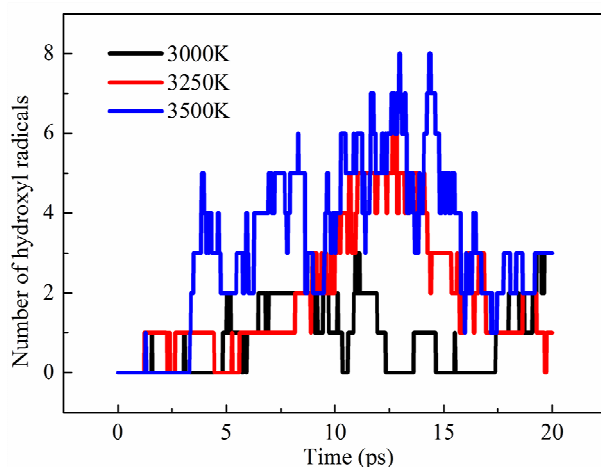
Figure 6. Distribution of hydroxyl radicals with time in the simulation of NOH-60 model at

3000 K (black), 3250 K (red) and 3500 K (blue), respectively.

Transformation to H_2O molecules: During the process of pyrolysis, hydroxyl radicals

react with phenolic hydroxyls and hydrogen free radicals, to generate H_2O molecules, which is

the main transformational way for hydroxyl radicals. At the initial stage of pyrolysis, H_2O

molecules, which are the first produced small oxygen-containing molecules, are formed in three

ways (Figure 7): i) the reaction between hydrogen free radicals and phenolic hydroxyl groups

(reaction 3); ii) the reaction between hydroxyl radicals and phenolic hydroxyl groups (reaction

4); iii) the reaction between hydrogen free radicals and hydroxyl radical (reaction 5). The results

also agree well with the regulation pattern in the novolac PR system found by Jiang et al.[10] and

Desai et al.[11]. Furthermore, as the temperature increasing, the possibility of occurrence of

reaction 4 and reaction 5 is increased in the system rich in hydroxyl radicals. According to the

distribution of produced H_2O molecules with time (Figure 8), more H_2O molecules are generated

at higher temperature. The beneficial impact of hydroxyl radicals to the production of H_2O

agrees well with Ouchi's [1] view that the more hydroxyl radicals in the samples, the more H_2O

molecules produced in the system. Nevertheless, the dependence of the number of H_2O

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molecules on the number of hydroxyl radicals is not obvious for the various generation ways of

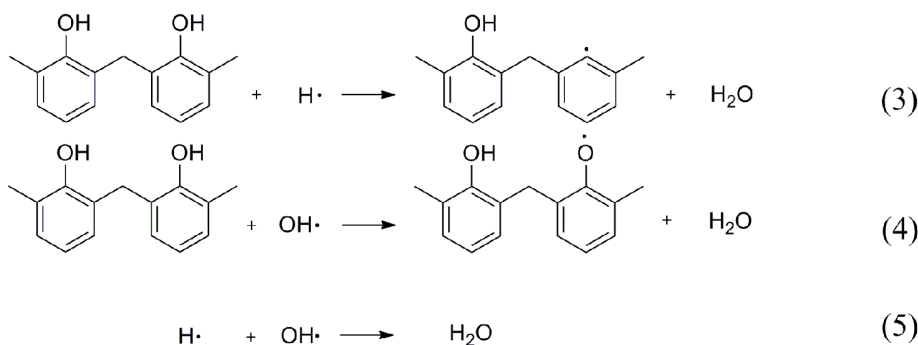H_2O molecules which would take part in the reaction again (Figure 8).

(3)

(4)

$$H\cdot \; + \; OH\cdot \; \longrightarrow \; H_2O \qquad\qquad (5)$$

Figure 7. Mechanism of H_2O molecules formation in the simulation of NOH-60 model at 3500
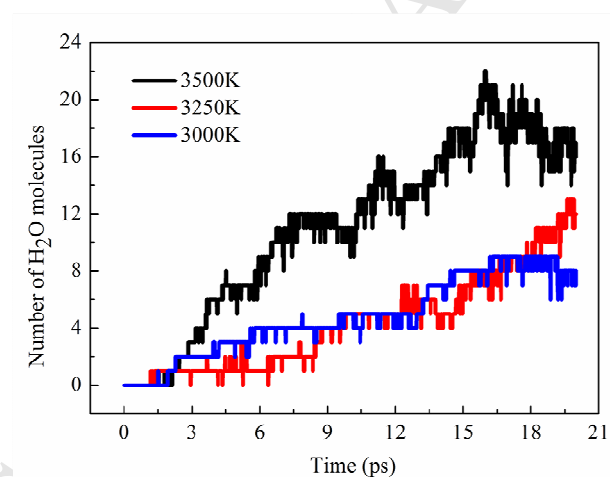
K.

Figure 8. Distribution of H_2O molecules with time in the simulation of NOH-60 model at 3000

K (blue), 3250 K (red) and 3500 K (black), respectively.

Transformation to CO_2 molecules: In our simulation, we observed that all CO_2 molecules

were generated from the reaction between hydroxyl radicals and CO from phenoxyl radicals (See

3.2.1) and the amount of CO_2 (Table 2) was greatly influenced by the number of hydroxyl

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radicals (Figure 6). This also agrees with Ouchi's research in novolac resin[20]. According to his view, CO would be further oxidized to CO_2 so the generation of CO should before that of CO_2. Nevertheless, it is still controversial for the opinion of Jackson et al.[3] that the hydroxyl methyl and methylene groups in cured PR would be oxidized to the carboxyl and carbonyl respectively. Considering that the decarboxylation reaction is easier than decarbonylation reaction, they hold the view that CO_2 may be produced before CO. One of the possible reasons for this difference is the absence of hydroxymethyl in our models, and it still require for more verification of experimental and theoretical studies.

Promotion to production of CO molecules: Although CO molecules can not be transformed directly from the hydroxyl radicals, the production of CO in above-mentioned evolution of the phenoxyl radicals can be promoted by hydroxyl radicals. The system rich in hydroxyl radical produces more CO molecules, because the hydroxyl radicals may involve in the oxidation of phenolic hydroxyl groups and generate phenoxyl radicals which would transform into CO molecules. In fact, with counting the amount of CO with time at different temperatures (Figure 9), we found that the distribution of CO present a similar varying pattern with temperature with that of hydroxyl radicals and both of them show maxima at 3500K. Nevertheless, the dependence of the number of CO molecules on the number of hydroxyl radicals is not obvious as CO molecules would be decomposed into radicals which can take part in the reaction again.
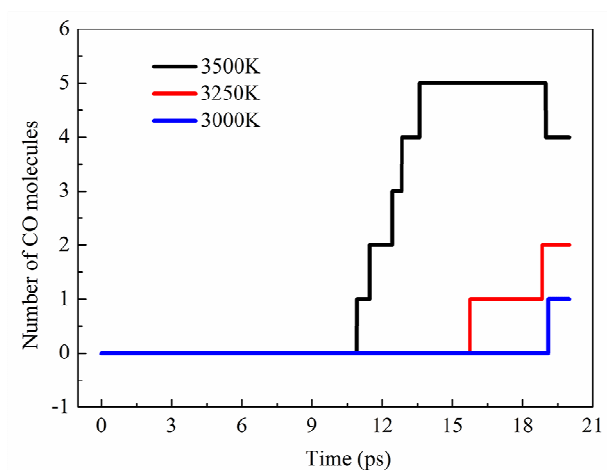
Figure 9. Distribution of CO molecules with time in the simulation of NOH-60 model at 3000 K (blue), 3250 K (red) and 3500 K (black), respectively.

3.3 Influence of evolving modes of phenolic hydroxyl groups to the backbone of PR

Based on above analysis, we found that the highly reactive phenolic hydroxyl group is the functional group first involved into pyrolysis reaction and produce hydrogen free radicals, phenoxyl radicals and hydroxyl radicals, thus initiating following reaction. Both the two above-mentioned evolution modes of phenolic hydroxyl groups (I. phenolic hydroxyl groups - phenoxyl radicals - small oxygen-containing molecules; II. phenolic hydroxyl groups - hydroxyl radicals - small oxygen-containing molecules) can lead to a great deal of damage to backbone of resin while from different aspects. Evolution mode I facilitates the transformation of backbone with reducing the stability of benzene ring by the dehydrogenation reaction of phenol ring. And evolution mode II can damage the structure of resin with oxidation of PR chains especially the oxidation of phenolic hydroxyl groups by hydroxyl radicals. From this point of view, the generation of phenoxyl radicals is the basic reason for the damage of the resin backbone.

From another aspect, we should point out the minor positive effect of phenolic hydroxyl groups to the thermal stability of resin at the initial stage of pyrolysis. The phenolic hydroxyl groups may dehydrate and produce ether linkage, especially the six-member ring ether (Figure 10), which enhance the thermal stability of resin by increasing of the cross-linker. When dehydrogenation occurred in the same constitutional unit, it means that the phenolic hydroxyl and methylene in the benzene rings connected directly and the dehydrogenation of both groups happened simultaneously. Other free radicals in the system may react with six-member ring ether, which can exist stably for a long time[11-12, 19, 25], give a temporary stability to the neighboring benzene ring. This effect is helpful to improve the thermal stability of resin at the initial stage of pyrolysis but it would gradually get weaker with the temperature rising or the time continuing. This also can be confirmed by the fact that the high-*ortho* novolac resins often exhibit good heat-resistant property in a certain sense.
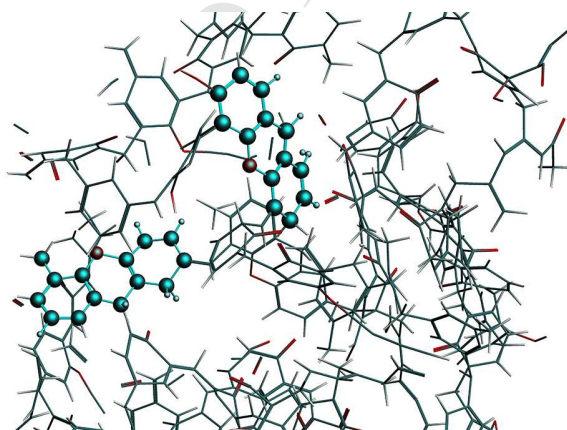

Figure 10. Snapshot of the simulated system after a 10-ps NVT-MD run in the simulation of NOH-60 model at 3500 K (the structure of six-member ring ether was highlighted by ball-and-stick models).

4. Conclusions

We have presented the simulation with ReaxFF for the initial stage of pyrolysis of cured PR especially the behavior of phenolic hydroxyl group under various temperatures and the formation mechanism of small oxygen-containing molecules. We observed that the highly active phenolic hydroxyl groups are easy to convert to phenoxyl radicals and hydroxyl radicals (primary evolution), and then the products of primary evolution transform into small oxygen-containing molecules (secondary evolution), with the amount of small oxygen-containing molecules increasing 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 (I. phenolic hydroxyl groups - phenoxyl 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. Thus, the phenolic hydroxyl group plays an important role in the process of resin pyrolysis and this could be valuable to the enhancement of the thermal stability and char yield of resin.

ACKNOWLEDGMENT

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