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The Influence of Oxygen on Thermal Decomposition Characteristics of Epoxy Resins Cured by Anhydride

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Abstract: Anhydride cured epoxy resins are always used as pivotal solid insulation medium in many electrical equipment, which will decompose due to the high temperature caused by partial discharge and the presence of oxygen will aggravate this process. In order to explore the influence of oxygen on the thermal decomposition characteristics of epoxy resin cured by anhydride, simulation models are established in this paper. The ReaxFF force field is used to simulate the pyrolysis process of epoxy resin and the changes in production of small molecular gases (such as CO₂, H₂O, CO and CH₂O), and C₂, C₃ are discussed. The results show that the oxygen will affect the main chain of the epoxy resin by introducing a carbon-oxygen double bond to the tertiary carbon atom attached to oxygen atom. Meanwhile, with the presence of oxygen, all the products' initial generation time will be earlier, the amount of CO₂ will increase, the amount of H₂O will go up dramatically while that of CH₂O remain basically unchanged, the types and quantities of C₂ and C₃ products increase obviously, mainly reflected in the oxygenated products.

Keywords: oxygen; epoxy resins; ReaxFF force field; thermal decomposition

1. Introduction

Anhydride cured epoxy resins are widely used in electrical equipment such as GIS, transformer, switchgear and cable termination because of its favorable insulating properties [1-2]. However, these resins are inevitable to defects, such as pits, contamination and metal particles during their manufacture, transportation, and operation because of electric, heat, and mechanical stresses. These defects render the surface of epoxy resins vulnerable to partial discharge, which can lead to an average temperature rise of 170 °C and maximum of 1000 °C around a volume of $5 \times 10^{-11} \text{ cm}^3$ on the epoxy resin surface near the partial discharge area [3-6]. High temperature can result in the decomposition of epoxy resin and seriously deteriorate their insulating and mechanical performance, and the presence of oxygen will aggravate this process [7-8].

Huy et al [9-11] conducted a series of studies on the thermos-oxidative aging of anhydride cured epoxy resin. They found that the process brings down the glass transition temperature and produces oxidized resultants, of which the depth follows an exponential distribution, the mass of the resins decrease by the quasi-hyperbolic function at the same time. Under the thermo-oxidative degradation, the aging process, crack growth and their interaction of epoxy resin were investigated by X. Colin et al. It was found that the crack will occur on the surface when the brittles of the oxide layer reaches a critical value [12-14]. J. Decelle [15] et al studied the mechanism of oxygen's effect on the network shrinkage during the thermal aging of aromatic diamine-cure bisphenol F epoxy resins and found that oxidizing the branched radical chain generated by the monomolecular decomposition of hydroperoxides is the main

path of oxygen consumption, as well as the reason of epoxy resins' mass loss. Yang et al.^[16] studied the effects of aging time and temperature on the thermal aging characteristics of anhydride cured epoxy resins. The results show that the surface molecular will rearrangement, their apparent free volume will reduce significantly and the bending strength will decline obviously due to thermal aging with the presence of oxygen.

Besides, effects of thermos-oxidative aging of epoxy resins on their electrical performance were studied as well. Jia et al.^[17] investigated the thermo-oxidative aging of insulating materials in high voltage switchgear and found that their dielectric properties will decrease at first, then increase and finally tend to stabilize. At the same time, oxygen will accelerate the aging process by the reaction with the weak bonds. The aging behavior under partial discharge of epoxy resins was studied by Hudon et al.^[18-19]. Some liquid substances (glyoxylic acid and glycolic acid) and solid substance (crystal of hydrated oxalic acid) are found in the experiment, and not only can the liquid lead to sharp increase in surface conductance, but also accelerate the deterioration of epoxy resin.

The ReaxFF reactive force brought forward by Duin and Dasgupta et al.^[20] developed rapidly in recent years. The force field parameters for different elements are exploited continuously and their application are extent to high-temperature reaction (pyrolysis, combustion and explosion) of organic molecules^[21-22], catalytic reactions^[23], nanotube formation^[24], kinetic process of anakinetomere^[25-26] and so on. Gregory^[27] used ReaxFF force field to simulate the mechanical properties of amino-cured epoxy resin and the results are in good agreement with the experimental ones. The pyrolysis of phenolic resins was studied by ReaxFF force field and the relationship between the amount of hydroxyl groups and the oxygenated products was investigated^[28]. Diao et al studied the pyrolysis mechanism of pure epoxy resin by ReaxFF force field and the formation of small molecules such as CH₂O, H₂O, CO and H₂ was explored^[29].

Based on the previous study^[30] on the decomposition mechanism of anhydride-cured epoxy resin, ReaxFF force field is used to analyze the influence of oxygen on the decomposition characteristics of epoxy resin through several simulation models to lay foundation for analysis of aging and failure of solid insulation in the electrical equipment.

2. Simulation Details

2.1 Introduction of ReaxFF Force Field

The traditional molecular force field method is unsuitable for simulating the chemical reaction process with continuous changes at the bond order due to its dependence on the bond order. To address this issue, Bond Order (BO) parameter is introduced to the ReaxFF force field, which allows for a continuous change in the bond order between atoms from unbonded to empiric bond order during the simulation. In the model of the reaction force field, the concept of atom type in the classical force field is not taken into consideration, there is no connectivity among the atoms in the system, either. Instead, the connectivity at the current moment depends on the BO between any two atoms. Expression of BO is the core of ReaxFF force

field, as shown in Eq. (1),

$$BO_{ij}^i = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi} = f(r_{ij}) \quad (1)$$

where r_{ij} is the distance between atom i and j , BO_{ij}^{σ} , BO_{ij}^{π} , $BO_{ij}^{\pi\pi}$ are single bond, double bond and triple bond respectively. Moreover, a function of the over-coordination of the central atom should be added to Eq. (1) to obtain the relationship between final BO and distance.

Based on the definition of BO, the interaction between atoms is defined as a function of BO, which is divided into bond, angle, dihedral angle, conjugation, coulomb, van der Waals and adjustment items through complicated function calculation. Energy of all parts in the system is described by BO except non-bond interaction, as shown in Eq. (2),

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{tors} + E_{conj} + E_{vdwaals} + E_{Coulomb} \quad (2)$$

During the simulation, ReaxFF force field describes the chemical bond rupture and formation by calculating the variation of BO with the distance in each simulation time step iteration.

2.1 Simulation Steps

The structure used in this paper is the noncross-linked epoxy resin formed by the dehydration condensation of two bisphenol A diglycidyl ether molecules^[31], as shown in Figure 1 (where α and β are the carbon atoms). There are four simulation models, the first one consists of 15 epoxy molecules and the other three contain 3, 5, 10 more oxygen molecules respectively.

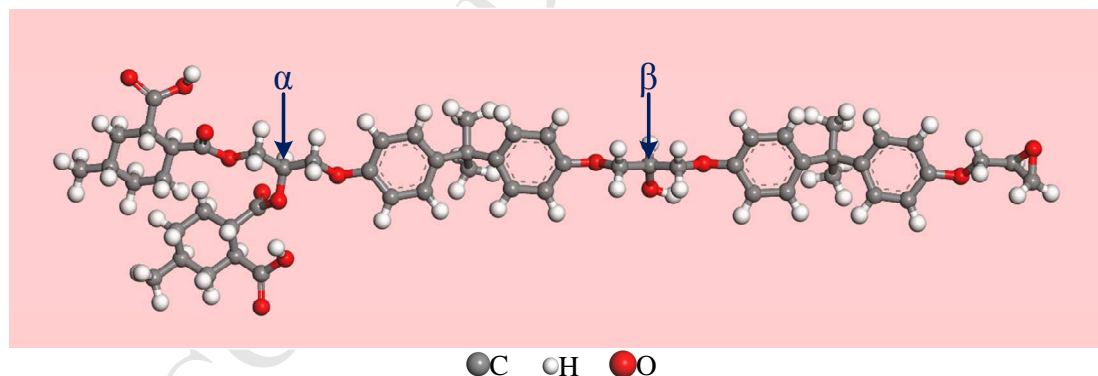


Figure 1 Structure of epoxy resin

Table1 Construction of models

Number	Initial Structure	Initial Density g/cm ³	Density after GM g/cm ³	Final Structure
1				15*C ₅₇ H ₇₀ O ₁₄
2	15*C ₅₇ H ₇₀ O ₁₄	0.5	1.17	15*C ₅₇ H ₇₀ O ₁₄ +3O ₂
3				15*C ₅₇ H ₇₀ O ₁₄ +5O ₂
4				15*C ₅₇ H ₇₀ O ₁₄ +10O ₂

The simulation steps are as follow,

1) Build three dimensional periodic models at first, of which the initial densities

were set to 0.5g/cm^3 ;

- 2) Annealing was then performed, balance the model with NVT ensemble and NPT ensemble under 600K for 100ps, and then repeat this step by reducing the temperature in a gradient of 50K until temperature was 300K(room temperature);
- 3) Geometry optimization was used to get a more stable structure, after which the density is 1.17g/cm^3 , as shown in Table 1;
- 4) The simulation of thermal decomposition came last, NVT ensemble was used and the temperature was set at 1300K (the highest temperature during the real partial discharge), the time step was 0.1fs and the simulation lasted for 1000ps.

3. Results and Discussion

3.1 Products of epoxy decomposition

According to the previous research^[16,29,20,36], as for the decomposition products of anhydride-cured epoxy, the major small molecular gas products are CO_2 , CO , CH_2O and H_2O , as shown in Figure 2. The main sources of CO_2 and CO are the acyl oxygen bonds, while CH_2O is from epoxide groups. H_2O are produced by elimination of hydroxyl groups as well as collision of hydroxyl radicals and free hydrogen atoms. C_2 and C_3 are the decomposition of six-membered rings in the anhydride and the carbon chain do not contain benzene rings.

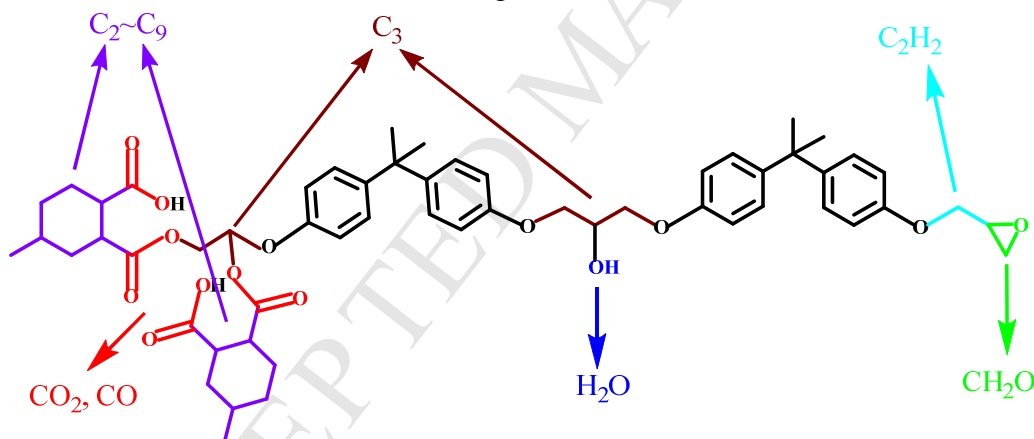


Figure 2 Products of epoxy decomposition

3.2 Consume of reactants

In Figure 3 and 4, oxygen molecules are consumed from 28.5ps to 300ps and the main chains of epoxy begin to break earlier with the addition of oxygen. When there are ten oxygen molecules, the initial breaking time of epoxy advances from 65ps to 34ps, indicating that oxygen can promote the main chains cleavage of epoxy. The tertiary carbon atoms connected to oxygen atoms are prone to be oxidized to acyloxy groups by oxygen, especially the α and β position in Figure 1.

3.3 Formation of small gases

In Figure 5, the initial generation time of CO_2 is advanced and its output increases with the growth of oxygen. The hydroxyl groups can be oxidized to carboxyl groups, while the tertiary carbon atoms connected to oxygen atom can be oxidized to acyloxy with the presence of oxygen, both of which contribute to the increase of acyloxy groups. Besides, the free oxygen atoms will react with CO and

produce CO_2 , resulting in the increase of CO_2 . In Figure 6, when there are oxygen molecules, CO molecules exist unsteadily but consumed constantly, and this process will be more frequent as the oxygen increase.

Seen from Figure 7, the production of water goes up significantly with the addition of oxygen because of combination of free oxygen atoms and free hydrogen atoms. However, water production tends to saturate with the increase of oxygen molecules due to limitation of simulation temperature and time. On the other hand, the formation of CH_2O remains basically unchanged on account of that CH_2O is entirely produced by epoxy groups and the oxygen has little effect on this process, as shown in Figure 8.

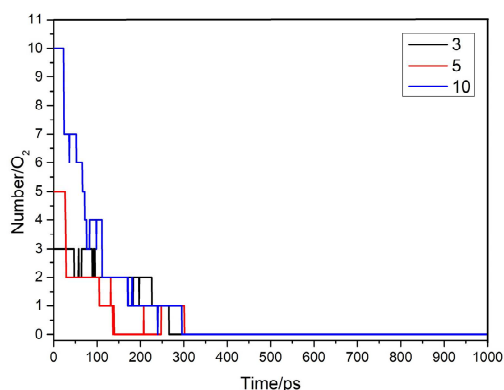


Figure 3 Time evolution of oxygen molecules

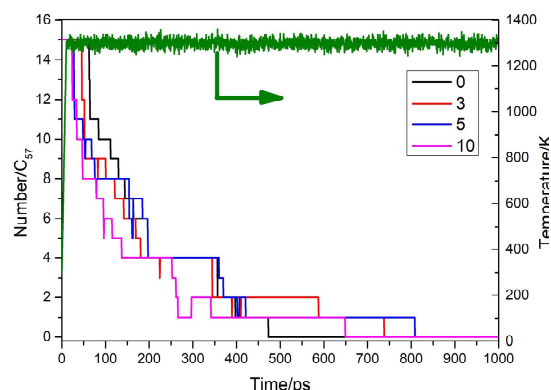
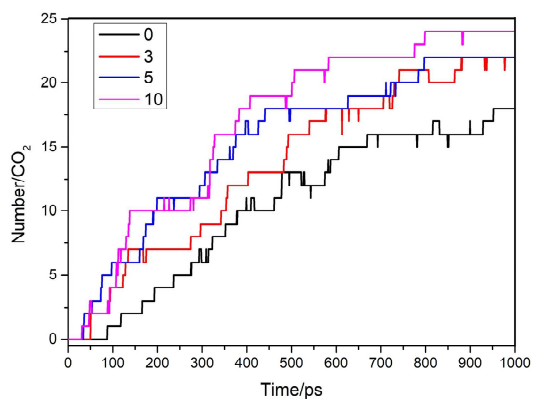
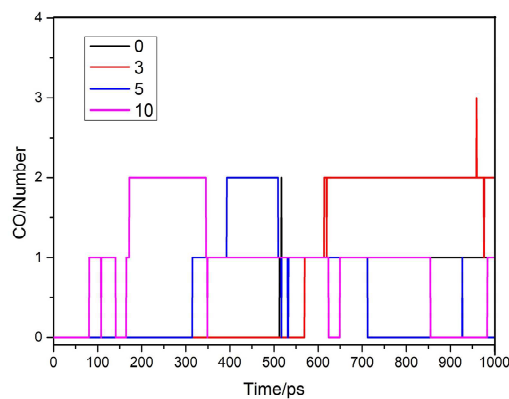
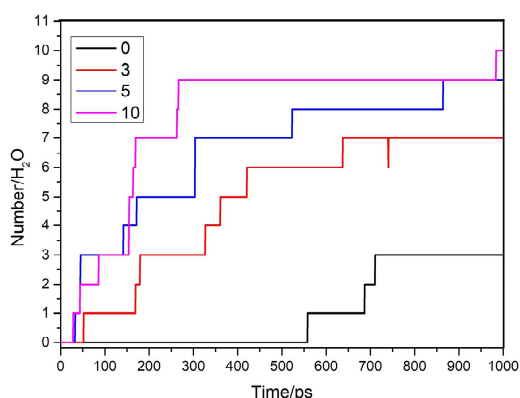
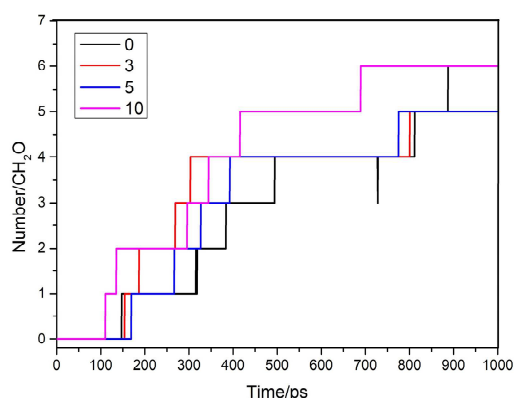


Figure 4 Time evolution of epoxy molecules

Figure 5 Time evolution of CO_2 Figure 6 Time evolution of CO

Figure 7 Time evolution of H₂OFigure 8 Time evolution of CH₂O

Seen from Figure 5, 6, 7 and 8, when there are no oxygen, the production of small molecule gases has the following sequence: CO₂, CH₂O, CO, and H₂O. When oxygen exists, CO₂ is still the earliest while the initial generation time of H₂O is earlier than that of CO and CH₂O. When there are 10 oxygen molecules in simulation model, the sequence of initial generation time changes into CO₂, H₂O, CO and CH₂O, and the most abundant gas products is still CO₂ while the second one changes from CH₂O to H₂O, and CO comes the least as before.

3.3 Formation of C₂ and C₃ products

The formation of C₂ and C₃ are shown in Figure 9 and 10. It is obviously that the yields of C₂ and C₃ products increase with the addition of oxygen and its amount. Seen from Table 2, ethylene and vinyl alcohol radicals are the main C₂ products during the epoxy decomposition without oxygen. By contrast, the number and type of C₂ products increase greatly with the presence of 10 oxygen molecules, mainly reflected in more oxygen-containing C₂ groups or compounds, including acetic acid, acetic acid radicals, acetaldehyde groups and formic anhydride radicals. In the view of initial generation time, C₂H₂O is the earliest products whether there are oxygen molecules or not, but that of C₂H₂O advanced greatly, from 311ps to 43ps.

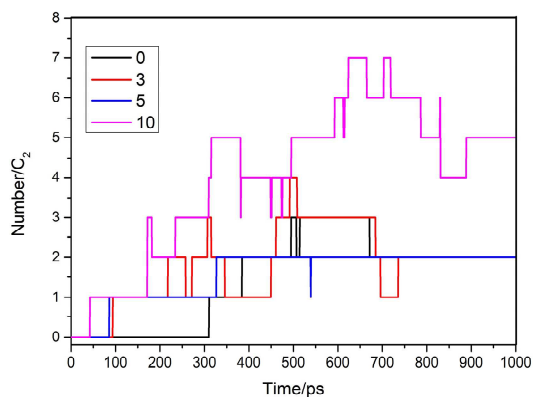
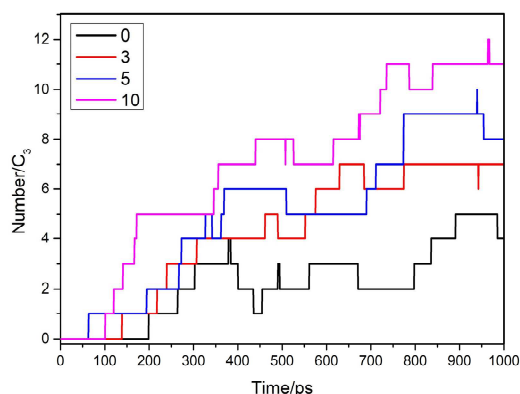
Figure 9 Time evolution of C₂Figure 10 Time evolution of C₃

Table 2 Information of C₂ products

Product	Number of Oxygen	Products	Initial Generation Time	Consume Time	Maximum	Final Number	Structure
C ₂	0	C ₂ H ₂ O	311ps	—	2	2	•HC=CH-O•
		C ₂ H ₃	335ps	671.5ps	1	0	H ₂ C=CH•
		C ₂ H ₃ O	512ps	531ps	1	0	•HC=CH-OH
	10	C ₂ H ₂ O	43ps	—	4	2	•HC=CH-O• O=C=CH ₂
		C ₂ H ₃ O	86.5ps	224.5ps	1	0	H ₂ C=CH-O•
		C ₂ H ₃ O ₂	183.5ps	235ps	1	0	•CH ₂ -C(=O)-OH
		C ₂ H ₃	316ps	—	2	1	H ₂ C=CH•
	C ₂ O ₃	623ps	—	1	1	•C(=O)-O-C(=O)•	
	C ₂ H ₄ O ₂	704.5ps	—	1	1	H ₃ C-COOH	

4. Analysis of reaction paths

Partial reaction paths where oxygen has influence on the epoxy decomposition mechanism is shown in Figure 11. P₁, P₂, P₃ and P₄ show the influence on breakage of main chain of epoxy, in which P₁, P₂ and P₃ introduce a carbon-oxygen double bond to the tertiary carbon atom attached to oxygen atom at the position of α while P₄ does at the position of β [32-35]. The activation energy of C—O bond linked to α is 186.58kJ/mol, the lowest during epoxy decomposition without oxygen, resulting in the most vulnerable to breakage of this C—O bond. When oxygen participates in the reaction, the activation energies of P₁, P₂, P₃ and P₄ are 137.35 kJ/mol, 175.87 kJ/mol, 160.24 kJ/mol and 151.02 kJ/mol respectively, of which all are lower than that of C—O, thus advance the initial fracture of epoxy main chain.

The product M of P₁ can decompose into CO₂ and cycloalkane through the reaction paths of P₁₁ and P₁₂ without oxygen as well as diolefin and product N through P₁₃. Then vinyl alcohol free radicals, CO₂, and CO are produced by the decomposition of product N through P₁₄ and P₁₅ [36]. With the presence of oxygen, the P₁₃ is promoted because of the tertiary carbon linked to oxygen atoms at the position of α_1 and α_2 . When the reaction takes place at α_1 (P₁₆), product N will decompose into vinyl alcohol free radicals and CO₂; when at α_1 (P₁₇), a carbon-oxygen double bond-containing unstable product and CO₂ will be produced, which is the reason why there are more C₂H₂O radicals and the initial generation time advances greatly. One of the products of P₂ and P₃ contains the structure of formic anhydride, which can produce formic anhydride. And P₄₁ is the main formation path of acetic acid radicals.

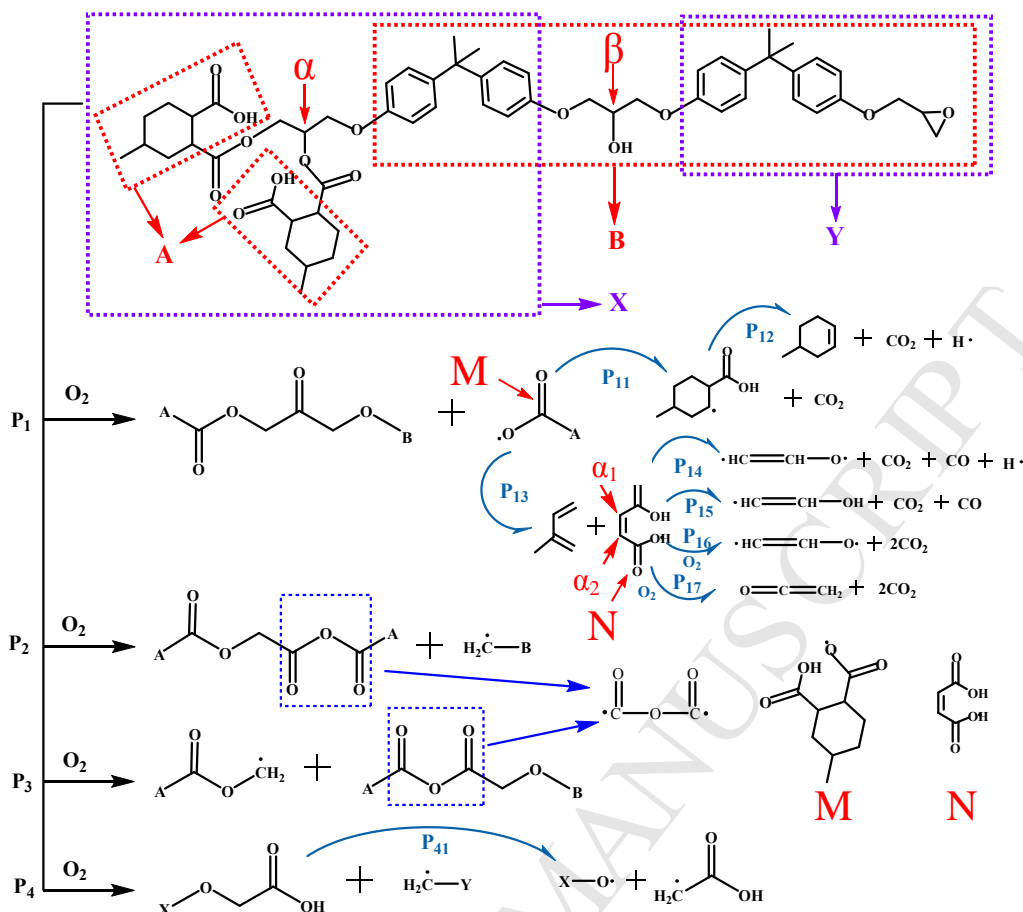


Figure 11 Reaction paths of oxygen

5 Conclusion

ReaxFF force field was used to simulate the influence of oxygen on thermal decomposition characteristics of epoxy resin cured by anhydride, the changes in production of small molecular gases and C₂, C₃ products were discussed as well as the formation paths. The conclusions are as follow,

- 1) Presence of oxygen changes the main chain breakage of epoxy under high temperature mainly by introducing carbon-oxygen double bond to the tertiary carbon atoms linked to oxygen atom, leading to advance in initial break time of the main chain;
- 2) With the presence of oxygen, the yield of CO₂ increases, the amount of H₂O goes up sharply while that of CH₂O remains basically unchanged. The sequence of initial generation time changes into CO₂, H₂O, CO and CH₂O and the initial generation time are all earlier.
- 3) With the presence of oxygen, the types and quantities of C₂ and C₃ products increase obviously, mainly reflected in the oxygenated products, the initial generation time is earlier as well.

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Conflicts of Interest

The authors declare no conflict of interest.

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Highlights

- Oxygen will bring forward the initial fracture of epoxy main chain.
- Presence of oxygen advance the initial generation time of gas products.
- Presence of oxygen increases the production of CO₂ and H₂O.
- Types and quantities of oxygenated C₂ and C₃ products increase obviously.