Molecular Dynamics Simulation of Ceramic Polyolefin for Fire Resistant Cable

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Abstract. In order to study the mechanism of high temperature environment’s influence on the mechanical properties and interparticle interactions of ceramic polymer materials for fire-resistant cables, the typical models of three ceramic polyolefin Formulations were established according to the distribution proportion of each material. With the assistance of molecular simulation software, molecular dynamics simulation was carried out. The results show that with the increase of temperature, the intermolecular interaction weakens, the mechanical modulus decreases, and the FFV increases. The Formulation with the most significant intermolecular interaction at high temperature, the one with the largest mechanical modulus at the same temperature and the one with the slowest increase of FFV with temperature’s increase is the mixture system of ceramic ethylene butene copolymer and 28% EVA. The simulation results can provide reference for the selection of polyolefin ceramic materials for fire resistant cables.

Keywords: Fire resistant cable; Ceramic polyolefin; Molecular dynamics simulation; Material selection.

1. Introduction
In recent years, the proportion of power supply interruption caused by power cable fire accidents is rising, which makes the research, production and application of fire-resistant cable become a hot spot. Material selection is the key to the final performance of fire-resistant cable. Ceramic polymer material is a kind of material widely used in fire-resistant cable. It can form a layer of dense structure with ceramic framework in the open fire environment by doping ceramic forming agent, ceramic filler and other functional additives in the specific polymer matrix, so as to achieve the effect of air isolation and therefore, ensure the safe operation of the cable to the greatest extent[1].

Since 2004, when Hanu L G prepared ceramic polymer materials by adding fillers into rubber matrix, the research and application of ceramic polymer materials have been increasing[2]. In 2006, ceramic polymer materials were first produced in Australia[3-4]. As a branch of ceramic polymer materials, ceramic polyolefin materials are low-costing and have a wide application range. At present, PE, EPDM, PVC, EVA and PVAc are mainly used as rubber matrix in the preparation of ceramic polyolefin. The corresponding research in the world is mostly to explore the change law of mechanical properties and thermal stability under different proportions of different functional components. For example, Hassany Z found that the content of ceramic filler was positively correlated with the thermal
stability and Young's modulus of the ceramic PVAc[5]. Thomson et al. found that the ceramic material can not only effectively delay the heat transfer, but also reduce the emission of greenhouse gas and smoke[6]. LI Y M et al. found the best mass ratio of a kind of ceramic EVA to reach the best performance[7].

At present, in the field of electrical engineering, molecular dynamics simulation is mostly used to evaluate the running state of materials in key parts of power equipment, such as the research on the types of pyrolysis products of transformer insulating oil, insulating paper or the interface mixed system formed by them under overheating conditions to figure out their changing trend with time and temperature [8-11], or the diffusion behavior of small molecular gas in the system [12-13], or exploring the changing trend of typical solid insulation materials’ thermodynamical and mechanical properties, such as XLPE, under doping or external electric field[14-16], or the molecular simulation analysis on the insulation performance difference under different proportioning of several kinds of environmental protection insulation gas mixture system[17-19].

In view of the fact that most of the research on ceramic polyolefin materials for fire-resistant cables is based on experiments, this paper selects three Formulations of representative ceramic polyolefin materials, applying molecular dynamics simulation on the equivalent model with the assistance of material simulation software, and explores the influence of temperature on the mechanical properties of materials and the interaction mechanism between molecules. The relevant properties of the three materials are compared.

2. Modeling and Simulation

2.1. Basic Composition of Ceramic Polyolefin Formulation

The main composition and corresponding mass fraction of the three ceramic polyolefin Formulations involved in this paper are shown in the Table 1.

| Formulation identifier | Rubber matrix | Ceramic forming agent | Ceramic filler | Flame retardant |
|------------------------|---------------|-----------------------|---------------|-----------------|
| 1                      | 28%EVA/55%    | Glass powder/23%      | Mica powder/17%| Montmorillonite/5% |
| 2                      | EVA/30.06%    | Aluminum hydroxide/15.73% | Mica powder/26.15% | Ammonium polyphosphate/28.06% |
| 3                      | Ethylene-butene copolymer/35.36% | Aluminum hydroxide/22.22% | Silicon dioxide/17.17% | Magnesium hydroxide/20.2% |
|                        | 28%EVA/5.05%  |                       |               |                 |

The main components of glass powder are P₂O₅, accounting for 45.84%; Al₂O₃, accounting for 24.10%; K₂O, accounting for 14.32%; Na₂O, accounting for 10.16%; SiO₂, accounting for 5.58%. The main components of mica powder are SiO₂, accounting for 47.33%; Al₂O₃, accounting for 40.32%; K₂O, accounting for 12.35%.

2.2. Microscopic Modeling

According to the Formulations of ceramic polyolefin, the related monomer models were established by using molecular simulation software, and three kinds of amorphous cell models of ceramic polyolefin were generated.

Firstly, the long chain model of EVA (28% vinyl acetate contained), ethylene butene copolymer, ethylene propylene rubber, and ammonium polyphosphate was established and optimized.

Secondly, P₂O₅ molecular model, Mg²⁺ ion and OH⁻ ion models were established, and geometric optimization was carried out. What should be pointed out is that although magnesium hydroxide has a specific spatial configuration, when it and other specific substances form an amorphous cell model, the arrangement of Mg²⁺ and OH⁻ ions in space will be disordered. Therefore in this paper, the ion models
were directly established in substitution for magnesium hydroxide, with the charges arranged. Thirdly, K₂O, Al₂O₃ and Na₂O nanoclusters were established.

**Figure 1.** The microcosmic model of 28% EVA.  
**Figure 2.** The microcosmic model of Ethylene butene copolymer.

**Figure 3.** The microcosmic model of Ethylene-propylene rubber.

**Figure 4.** The microcosmic model of Ammonium polyphosphate.  
**Figure 5.** The microcosmic model of P₂O₅.  
**Figure 6.** The microcosmic model of Mg²⁺.  
**Figure 7.** The microcosmic model of OH⁻.

**Figure 8.** The microcosmic model of K₂O.  
**Figure 9.** The microcosmic model of Al₂O₃.  
**Figure 10.** The microcosmic model of Na₂O.  
**Figure 11.** The microcosmic model of Aluminum hydroxide.

2.3. Molecular Dynamics Simulation

Firstly, according to the composition ratio and material density of each Formulation, the amorphous cell was established at 298K, and the geometric optimization was carried out to obtain the model as shown in Figure 12 to Figure 14.

Secondly, the amorphous cell model obtained by geometric optimization was annealed, and then the NPT ensemble was used for relaxation. Then, the 150 ps and 200 ps molecular dynamics simulations were carried out at 1273K. NVT and NPT were selected as the ensemble, Andersen method was selected as the temperature-control strategy and Berendsen method was selected as the pressure-control strategy. For the non-bond energy terms, atom based method is used for van der Waals term and Ewald method is used for electrostatic interaction term’s calculation;

Thirdly, with 100K as the gradient, NVT was selected to cool down the cell for 150 ps, and then NPT ensemble was selected to equilibrate the cell for 200 ps. Then the models after molecular dynamics relaxation at 673K, 773K, 873K, 973K, 1073K, 1173K and 1273K were obtained;

Finally, the mechanical properties, CED and FFV of the models at different temperatures were
calculated.

Figure 12. The amorphous cell of ceramic EVA.

Figure 13. The amorphous cell of ceramic Ethylene-propylene rubber.

Figure 14. The amorphous cell of the mixture of ceramic ethylene-butene copolymer and 28% EVA.

3. Analysis of Simulation Results

3.1. Mechanical Properties

According to the generalized Hooke's law, the forces $F_1$, $F_2$ and $F_3$ acting on a certain volume element material can be equivalently decomposed into normal stress $\sigma_{xx}$, $\sigma_{yy}$ and $\sigma_{zz}$ and tangential stress $\tau_{xy}$, $\tau_{yz}$ and $\tau_{xz}$. The resultant tensor matrix is shown below.

$$
\sigma_{ij} = \begin{bmatrix}
\sigma_{xx} & \tau_{xy} & \tau_{xz} \\
\tau_{yx} & \sigma_{yy} & \tau_{yz} \\
\tau_{zx} & \tau_{zy} & \sigma_{zz}
\end{bmatrix}
$$

(1)

Assuming that the material is isotropic, in the stress tensor matrix, $\tau_{xy} = \tau_{yx}$, $\tau_{yz} = \tau_{zy}$, $\tau_{xz} = \tau_{zx}$, so there are only six independent components in the stress tensor matrix. The first one corner marker corresponds to the normal direction of the shear stress plane, and the latter corresponds to the actual direction of stress. At the same time, the strain tensor matrix corresponding to the strain component caused by each stress component is

$$
\varepsilon_{ij} = \begin{bmatrix}
\varepsilon_{xx} & \gamma_{xy} & \gamma_{xz} \\
\gamma_{yx} & \varepsilon_{yy} & \gamma_{yz} \\
\gamma_{zx} & \gamma_{zy} & \varepsilon_{zz}
\end{bmatrix}
$$

(2)

For isotropic materials, $\gamma_{xy} = \gamma_{yx}$, $\gamma_{yz} = \gamma_{zy}$, $\gamma_{xz} = \gamma_{zx}$, so there are only six independent components.

$$
E = \frac{\sigma_{xx} - \nu(\sigma_{yy} + \sigma_{zz})}{\varepsilon_{xx}} = \frac{\sigma_{yy} - \nu(\sigma_{zz} + \sigma_{xx})}{\varepsilon_{yy}} = \frac{\sigma_{zz} - \nu(\sigma_{xx} + \sigma_{yy})}{\varepsilon_{zz}}
$$

(3)

$$
G = \frac{\tau_{xy}}{\gamma_{xy}} = \frac{\tau_{yz}}{\gamma_{yz}} = \frac{\tau_{xz}}{\gamma_{xz}}
$$

(4)

In equation, $\nu$ represents Poisson's ratio.

The volume modulus and shear modulus of the three Formulations are shown in Figure 15 and Figure 16 respectively.
It can be seen from Figure 15 and Figure 16 that with the increase of temperature, the bulk modulus and shear modulus of the three Formulations show a downward trend as a whole, which conforms to the law that the mechanical modulus of polymer changes with temperature, and Formulation 3 have the maximum values of bulk modulus and shear modulus at the same temperature. This shows that the brittleness of Formulation 3 is the strongest among the three Formulations.

3.2. Mechanism of Particle Interaction

In order to characterize the intermolecular force in ceramic polyolefin cell, Cohesive Energy Density was introduced[20].

\[ CED = \frac{H_V - R_T}{V_M} \]  

(5)

Where \( H_V \) is the molar evaporation heat, \( R_T \) is the expansion work done during vaporization, and \( V_M \) is the molar volume.

The variation of CED of the three Formulations with temperature is shown in Figure 17 and Figure 18.
because the energy of electrostatic interaction between Mg$^{2+}$ and OH$^{-}$ ions is the main factor contributing to the cohesive energy of its amorphous cell structure.

3.3. FFV

According to the free volume theory, the void in polymer is the basis of the diffusion of small molecule solute in polymer. In this paper, the Fractional Free Volume is introduced to evaluate the ability of different kinds of ceramic polyolefin to block gas permeation. The definition of FFV is shown in the equation 6.

$$FFV = \frac{V_f}{V_o + V_f} \times 100\%$$  \hspace{1cm} (6)

Where $V_o$ is the volume occupied by the particles and $V_f$ is the free volume.

The changes of free volume and occupied volume with temperature of the three Formulations are shown in Figure 19 to Figure 21, and the variation law of FFV is shown in Figure 22.

![Figure 19](image1.png)  \hspace{1cm} ![Figure 20](image2.png)  \hspace{1cm} ![Figure 21](image3.png)  \hspace{1cm} ![Figure 22](image4.png)

Figure 19. The occupied volume and free volume of Formulation 1.

Figure 20. The occupied volume and free volume of Formulation 2.

Figure 21. The occupied volume and free volume of Formulation 3.

Figure 22. The FFV of three Formulations.

It can be seen from the figures that with the temperature rising, the FFV of the three Formulations is rising, and the increase of FFV is mainly caused by the increase of free volume. Among the three Formulations, the FFV of Formulation 3 was the lowest at higher temperature, and its growth rate was the slowest with the temperature rise. This indicates that Formulation 3 has the strongest ability to resist the flammable or combustion-supporting gas molecules in high temperature.
4. Conclusion
In this paper, three representative ceramic polyolefin Formulations were selected, and through molecular dynamics simulation, the mechanical properties, intermolecular interaction mechanism and FFV changing with temperature were obtained. Firstly, the bulk modulus and shear modulus of the three ceramic polyolefin Formulations decrease with the increase of temperature, which is in line with the change law between the polymer modulus and temperature. At the same time, the mixture system of ceramic ethylene butene copolymer and 28% EVA has the maximum mechanical modulus at the same temperature. Secondly, the CED of three ceramic polyolefin Formulations decreased with the increase of temperature. The results show that the CED of the mixture system of ceramic ethylene butene copolymer and 28% EVA is the largest, while its downward trend is the most obvious. Thirdly, the changing trend of FFV of three ceramic polyolefin Formulations was increasing with temperature, and the FFV of the mixture systems of ceramic ethylene butene copolymer and 28% EVA showed the least significant change trend with temperature. Based on the simulation results of mechanical properties, the interaction mechanism between particles and free volume distribution, it is considered that the mixture system of ceramic ethylene butene copolymer and 28% EVA have the best performance among the three Formulations, which is an ideal ceramic polyolefin material.

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References
[1] Ke R L, Zou X, Wang J H & L. Y. Shi,(2018) Research progress of ceramic polymer composites. Insulating Materials(12), pp. 1-5+10.
[2] Hanu L G, Simon G P & Cheng Y B, (2005) Preferential orientation of muscovite in ceramifiable silicone composites. Materials Science and Engineering A(1-2), pp. 180-187.
[3] Li H J, Guo J H, Zeng X R, (2015) Research progress of ceramic polymer. Special rubber products(4), pp. 67-72.
[4] Perera D, (2014) Ceramics research development and manufacture in Australia. Journal of the Australian Ceramics Society(1), pp. 49-68.
[5] Hassany Z, Genovese A & Shanks R A, (2010) Fire-retardant and fire-barrier poly(vinyl acetate) composite for sealant application. Express Polymer Letters(2), pp. 79-93.
[6] Thorson K, Rodrigo D & Preston C, (2006) In the Firing Line. European Coatings Journal(12), pp. 34-42.
[7] Li Y M, Deng C & Wang Y Z, (2016) A novel high-temperature polymeric material for cables and insulated wires via the ceramization of mica-based ceramifiable EVA composites. Composites Science and Technology(132), pp. 116-122.
[8] Zeng Y F, Wu G N & Yang Y, (2020) Study on the mechanism of high temperature pyrolysis and water content of silicon insulating oil based on molecular simulation. Proceedings of The Chinese Society for Electrical Engineering(4), pp. 1369-1377+1427.
[9] Li J C, Chen J M, Zhu M X & Zhang H Y, (2019) Pyrolysis mechanism of transformer oil paper insulation based on molecular dynamics simulation. Insulating Materials(6), pp.79-85+91.
[10] Wang X L, Li Q M, Zhang Y, Yang R & Gao S G, (2017) Molecular dynamics simulation of high temperature pyrolysis of transformer oil and influence mechanism of acid in oil. High Voltage Engineering(1), pp. 247-255.
[11] Yan J Y, Wang X L, Li Q M, Zhou Y, Wang Z D & Li C R, (2015) Molecular dynamics simulation of high temperature pyrolysis of insulating paper. Proceedings of The Chinese Society for Electrical Engineering(22), pp. 5941-5949.
[12] Liao R J, Gong C Y, Zhou X, Yang L J & Duan L, (2012) Diffusion behavior of small gas molecules in oil paper insulation system based on molecular dynamics simulation. *High Voltage Engineering*(09), pp. 2373-2382.

[13] Li Y S, Liu Z P, Hua X, Dai Y P & Shen X R, (2018) Molecular dynamics simulation of diffusion behavior of small and high molecular acids in oil. *Insulating Materials*(09), pp. 70-75.

[14] Li Y S, Hua X, Dai Y P, Liu Z P & Wang C J, (2019) Study on molecular structure change and electrical aging mechanism of XLPE dielectric materials under external electric field. *Journal of Atomic and Molecular Physics*(3), pp. 413-420.

[15] Li Y S, Zhang X B, Huang T H, Meng F Q & Xie Y L, (2019) Study on molecular structure change and electrical aging mechanism of XLPE dielectric materials under external electric field. *Journal of Molecular Science*(3), pp. 209-215.

[16] Shao S, He J L, Yu Y S, Duan Q J Liang S D & Xie Q (2020) Molecular dynamics simulation of thermodynamic properties of epoxy resin / anhydride system. *Insulating Materials*(8), pp. 38-43.

[17] Chen H, Li D B, Yu L, Yang H G, Tian Y Y, Yuan S X & Liu D P(2019) Molecular dynamics based SF\(_6\)/N\(_2\) Theoretical study on diffusion characteristics of gas mixtures. *Industrial Safety and Environmental Protection*(12), pp. 33-35.

[18] Zhang X X, Chen Q, Li Y, Xiao S, Zhang J & Liu C(2018) Decomposition mechanism of environmental friendly insulating medium C\(_3\)F\(_7\)CN / CO\(_2\). *Proceedings of The Chinese Society for Electrical Engineering*(24), pp. 7174-7182+7444.

[19] Li X, Li Y Y & Li Q K(2018) Temperature and different volume fraction SF\(_6\)/N\(_2\) Molecular simulation study on the effect of gas mixture on insulation capacity. *Journal of electric power*(3), pp. 221-228.

[20] Almasi M(2020) Cohesive energy density and internal pressure of benzene and 1-alkanol binary mixtures. *Journal of Molecular Liquids*().