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Yushun Zhao, Yufan Xu, Hao Shen, Bin Du, G. Teysseire. Introducing Chlorine into Epoxy Resin to Modulate Charge Trap Depth in the Material. *IEEE Transactions on Dielectrics and Electrical Insulation*, 2022, 29 (5), pp.1666-1674. 10.1109/tdei.2022.3191963 . hal-03785597

**HAL Id: hal-03785597**

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Submitted on 23 Sep 2022

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# Introducing Chlorine into Epoxy Resin to Modulate Charge Trap Depth in the material

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To cite: Y. Zhao, Y. Xu, H. Shen, B. Du, G. Teyssède, "Introducing chlorine into epoxy resin to modulate charge trap depth in the material", IEEE Trans. Dielectr. Electr. Insul. 2022 DOI: 10.1109/TDEI.2022.3191963

**Abstract**—The epoxy insulators in DC gas insulated transmission lines (GIL) tend to accumulate surface charges, which causes insulation flashover. Increasing the surface conductivity of epoxy resin, which can restrain the accumulation of surface charges on the epoxy insulator, is a potential method to improve the insulation performance of DC GIL insulators. The conductivity of polymer dielectric is strongly influenced by the charge trap characteristics of the polymer. In this work, we introduce chlorine with strong electronegativity and a larger atomic radius into the epoxy group segment of epoxy resin to improve the distributed energy level structure, which in turn reduces the electron trap depth, so as to increase the surface conductivity of epoxy insulating material without affecting its intrinsic dielectric strength. Based on the results of quantum chemistry calculation, the modulation laws of introduced chlorine (including the chlorine in form of hydrolyzable chlorine atom and non-hydrolyzable chlorine atom) on distributed energy levels of epoxy resin molecule are anticipated. These laws are explained from the microscopic perspectives of electron energy structure and electron cloud offset. Both the inductive effect of the chlorine atom and the conjugation effect of 2p electron orbital of oxygen atom in epoxy group impact the distributed energy levels through changing the spatial distribution of electron cloud density between and on valence bonds.

**Index Terms** — Charge trap depth, DFT, electrical conductivity, epoxy resin, quantum chemical calculation

## I. INTRODUCTION

Epoxy resin insulation material is used as a kind of polymer dielectric for DC gas insulated transmission lines (GIL), but its interface with SF<sub>6</sub> gas tends to accumulate charges, resulting in electric field distortion and insulation flashover [1]. The surface charge accumulation and electric field distortion can be restrained by increasing the surface conductivity of epoxy resin, which will achieve the purpose of improving the insulation performance of DC GIL insulators [2]. The conductivity of polymer dielectrics depends on the charge transfer rates in the polymer. Studies have shown that the transfer process of space charges in polymer dielectrics is strongly influenced by the distribution of charge traps in polymer molecular chains [3-12]. When the space charges are transferred to the polymer, they are trapped by deep and shallow traps in the molecular chain [13].

After these trapped charges are excited by enough energy, from thermal, electrical or radiative source, they can escape from the traps and move to the groups adjacent to the trap sites [14, 15]. Then the process of charges trapping and de-trapping is repeated to form conduction.

Many scholars introduce strong electronegative fluorine into polymer molecules to improve the trap characteristics and increase the surface conductivity of polymers. J. Li et al investigated the modulating mechanism of the fluorination treatment to the surface charge transfer on epoxy resin through quantum chemical calculation (QCC) analysis. The results show that the fluorination treatment generates shallow trap sites on the epoxy material surfaces, which improves the surface conductivity and subsequently accelerates the process of surface charge dissipation [16]. S. Akram et al modified the polyimide film surface with fluorine gas-phase and investigated the surface conductivity of fluorinated polyimide films. They found that the strong electronegativity of fluorine on the surface increased the polarity level of C-F bonds and decreased the surface charge trap density, thus improving the surface conductivity of fluorinated polyimide films [17]. H. Ruan et al introduced fluorine components into the surface layer of micron alumina epoxy (Al<sub>2</sub>O<sub>3</sub>/ER) composites by the fluorine-containing release agent (F-RA) with high transfer property, and investigated the effect of introduced fluorine on surface conductivity of the epoxy composites. The analyzed results show that the introduction of surface fluorine reduces the deep trap density and increases the shallow trap density on the surface of Al<sub>2</sub>O<sub>3</sub>/ER composites, which improves the surface conductivity of the composites [1].

The above methods of introducing fluorine into polymer molecules to modulate the trap characteristics and surface conductivity have been researched by many scholars, and positive research results have been obtained. However, fluorine is a strongly electronegative element with a small atomic radius, that easily generate hydrogen bonds in epoxy polymers. The hydrogen bonds will disturb the precise modulation on charge trap depth, which makes it difficult to explore the modulation laws of strongly electronegative elements on the electrical conductivity of the polymers.

The epoxy group segment of bisphenol-A type epoxy resin (DGEBA) polymer molecule has a high electron barrier, which makes the DGEBA molecule have a deep electron trap depth.

Based on the summary and analysis of the works done by above scholars, we introduced chlorine into the epoxy group segment of DGEBA molecule. On the one hand, the chlorine is a strongly electronegative element that can reduce the electron barrier height in epoxy group segment through inductive effect, thus shallowing the electron trap depth for the molecule containing chlorine. On the other hand, the chlorine has a larger atomic radius, which makes it difficult for chlorine to generate hydrogen bonds in epoxy polymers. Therefore, the surface conductivity of epoxy resin insulating materials can be improved through precisely modulating the charge trap depth of the molecule.

In this paper, through the comparison of distributed energy levels of geometrically optimized DGEBA molecule, the molecule introduced with a chlorine atom, and the molecule introduced with two chlorine atoms, we found the modulation laws on molecular orbital energy levels and charge trap depth induced by chlorine. This paper focuses on explaining the modulation laws from the perspectives of electron energy structure and electron cloud offset, expected to provide a theoretical reference for the structural design of polymer molecule and the modulation of molecular orbital energy levels.

## II. STUDY ON THE MODULATION LAWS OF INTRODUCED CHLORINE

### A. Structural Formulas for the Three Molecules

Fig. 1a shows the structural formula of DGEBA molecule. The epoxy group in DGEBA molecule has a strong reactivity and easy to be ring-opened and combined with other molecules under certain conditions.

Therefore, we introduced chlorine into epoxy group segment through the ring-opening reaction of the epoxy group. By opening the ring of an epoxy group in DGEBA molecule and connecting a chlorine atom to the methylene group after ring-opening, the chlorohydrin ether molecule with a chlorine atom introduced was obtained, called chlorohydrin ether A, as shown in Fig. 1b. Similarly, by opening the two epoxy groups in DGEBA molecule and connecting a chlorine atom to each of the two methylene groups after the ring-opening, the chlorohydrin ether molecule with two chlorine atoms introduced was obtained, called chlorohydrin ether B, as shown in Fig. 1c.

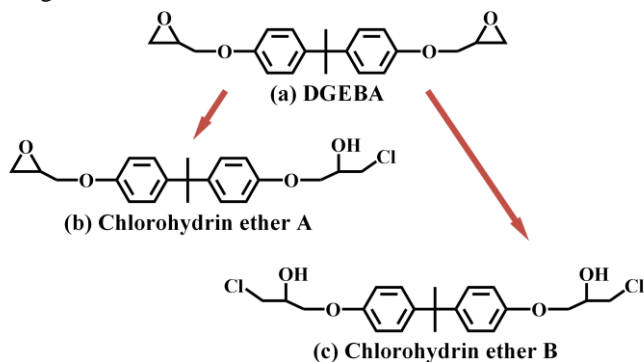


Figure 1. Molecular structures of the three molecules.

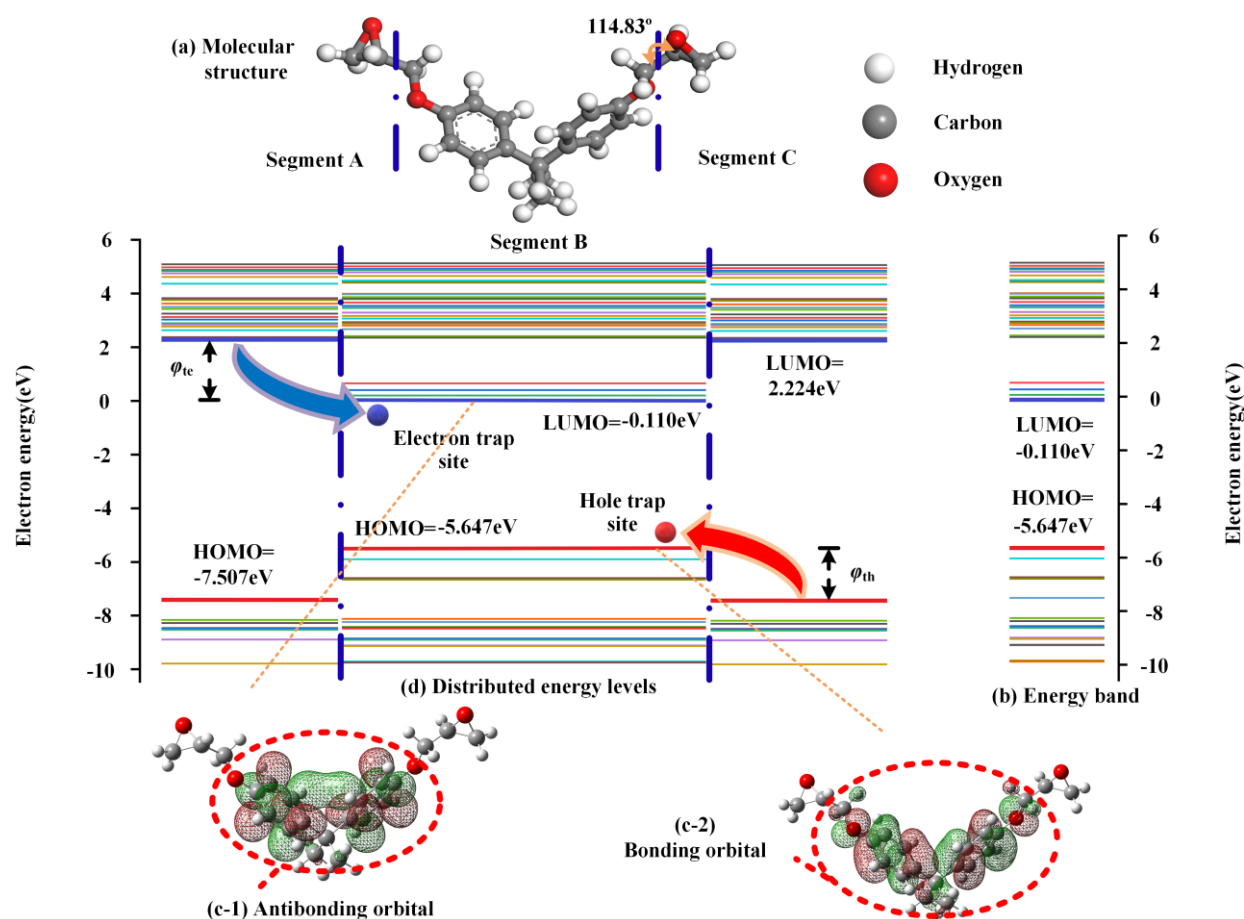
### B. Energy Band Structure and Distributed Energy Levels of DGEBA Molecule

In order to investigate the precise modulation of molecular orbital energy levels by chlorine, we considered here only the interactions of intra-chain atoms and without inter-chain atoms. Therefore, the energy band structure of the DGEBA molecule was calculated using Gaussian 09 software. We optimized the geometric structure of the DGEBA molecule using B3LYP hybrid functional method and 6-31 G(d) basis function set in density functional theory (DFT), with the program keyword set to “#opt b3lyp/6-31 g(d) geom=connectivity”, and the “charge” and “multiplicity” set to “0” and “1”, respectively. After the optimization, the output file of type “chk” was obtained. After opening the output file with GaussView software, we checked the bond angles through the “Angle properties” function and the energy level information through the “MOs” function. The energy band structure and distributed energy levels can be obtained, as shown in Fig. 2.

The structurally optimized DGEBA molecule is divided into three chain segments, as shown in Fig. 2a. The two parts composed of epoxy groups of DGEBA molecule are called segment A and segment C. The rest is the part consisting of a central carbon atom, two methyl groups and two benzene rings connected to the central carbon atom, two ether oxygen groups, and two methylene groups connected to the ether oxygen groups, which is called segment B. Fig. 2b shows the energy band diagram of DGEBA molecule, which has the LUMO energy level of -0.1110 eV and the HOMO energy level of -5.647 eV. The zero level in the band diagram is the vacuum level, as is the one in band diagrams below.

Fig. 2c-1 and Fig. 2c-2 show the distribution of molecular orbitals along the molecular chain corresponding to the LUMO energy level and HOMO energy level of DGEBA molecule, respectively. It can be seen that the molecular orbitals corresponding to the LUMO and HOMO energy levels of the DGEBA molecule are mainly distributed at the two benzene ring positions in segment B. Each carbon atom in the benzene ring contains a 2p orbital perpendicular to the plane of the benzene ring.

When the carbon atoms form bonds, these 2p orbitals are hybridized to form antibonding  $\pi$  orbitals ( $\pi^*$ ) and bonding  $\pi$  orbitals ( $\pi$ ). In the  $\pi^*$  system, the internuclear electron cloud of carbon atom with 2p orbital hybridization is sparse, and the energy of the  $\pi^*$  orbital formed by hybridization is higher. In the  $\pi$  system, the internuclear electron cloud of carbon atom with 2p orbital hybridization is dense, and the energy of the  $\pi$  orbital formed by hybridization is lower. In the antibonding orbital system of DGEBA molecule formed only by the hybridization of 2p orbitals of carbon atoms in benzene ring (Fig. 2c-1), the electron cloud between nuclei of the hybrid carbon atoms is sparse, and the energy of the  $\pi^*$  orbital formed by hybridization is higher, which is the energy corresponding to the LUMO energy level of DGEBA molecule. In the bonding orbital system of DGEBA molecule (Fig. 2c-2), in addition to the 2p orbitals of carbon atoms in the benzene ring, the 2p



**Figure 2.** The energy band structure and distributed energy levels of DGEBA molecule.

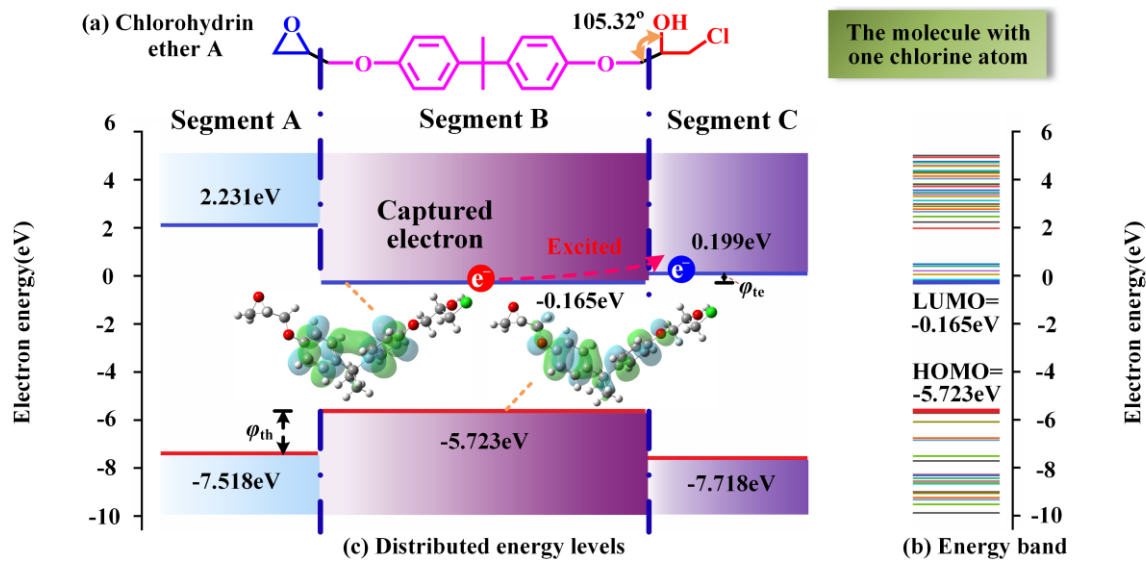
orbital of the central carbon atom of the DGEBA molecule, the 2p orbital containing lone pair electrons of the oxygen atom in the ether oxygen group and the 1s orbitals of the hydrogen atoms in methylene groups are also involved in hybridization of the bonding orbital, which increases the movement range of orbital electrons and averages the electron density in the bonding orbital system. Therefore, the energy of the hybrid molecular orbital in the bonding system is relatively low, which is the energy corresponding to the HOMO energy level of DGEBA molecule.

Fig. 2d shows the distributed energy levels of DGEBA molecule. The LUMO energy levels of segment A and segment C of the DGEBA molecule are the same, and the HOMO energy levels of segment A and segment C of the DGEBA molecule are also the same. It can be seen from the distributed energy levels of DGEBA molecule that the LUMO energy level and the HOMO energy level of segment B is the LUMO energy level and the HOMO energy level of the whole molecular chain, which corresponds to the fact that the hybrid molecular orbitals corresponding to the LUMO and HOMO energy levels of DGEBA molecule are only distributed on segment B. In order to transfer an excess electron captured by the LUMO energy level of segment B to other segments of DGEBA molecule, as shown in Fig. 2d, the trapped electron needs to overcome a high potential barrier, which means that the LUMO energy level of segment B is an electron trap site [18]. Similarly, in order to

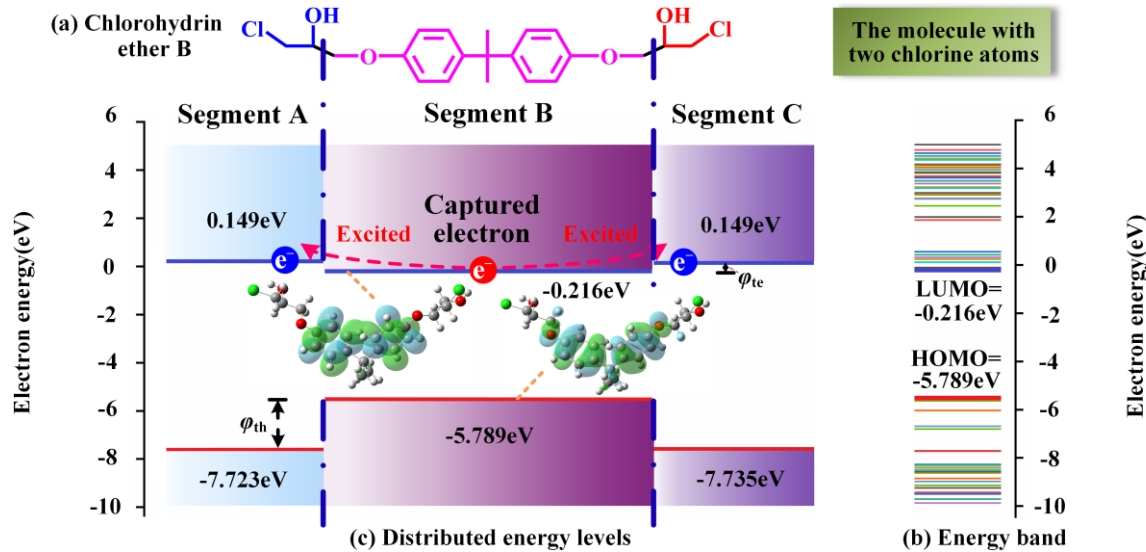
transfer the hole captured by the HOMO energy level of segment B to other segments of DGEBA molecule, the trapped hole also needs to overcome a high potential barrier, which means that the HOMO energy level of segment B is a hole trap site (shown in Fig. 2d). Therefore, the LUMO energy level of segment B is an electron trap energy level (the electron trap depth  $\varphi_{te}$  is 2.334 eV, which is the difference between 2.224 eV and -0.110 eV), and the HOMO energy level of segment B is a hole trap energy level (the hole trap depth  $\varphi_{th}$  is 1.860 eV, which is the difference between -5.647 eV and -7.507 eV).

### C. Comparison of Distributed Energy Levels of the Three Molecules

Using the same calculation method as above, we obtained the energy band structure and distributed energy levels of chlorohydrin ether A and chlorohydrin ether B molecules, as shown in Fig. 3 and Fig. 4, respectively. It can be seen that the distribution of the molecular orbitals corresponding to the LUMO and HOMO energy levels of both chlorohydrin ether A and chlorohydrin ether B molecules have no change compared with that of DGEBA molecule. Similar to the DGEBA molecule, the LUMO energy level and HOMO energy level of segments B of chlorohydrin ether A and chlorohydrin ether B molecules are the electron trap energy level and the hole trap energy level, respectively, which determine the LUMO and HOMO energy levels of the whole molecule.



**Figure 3.** The energy band structure and distributed energy levels of chlorohydrin ether A molecule.

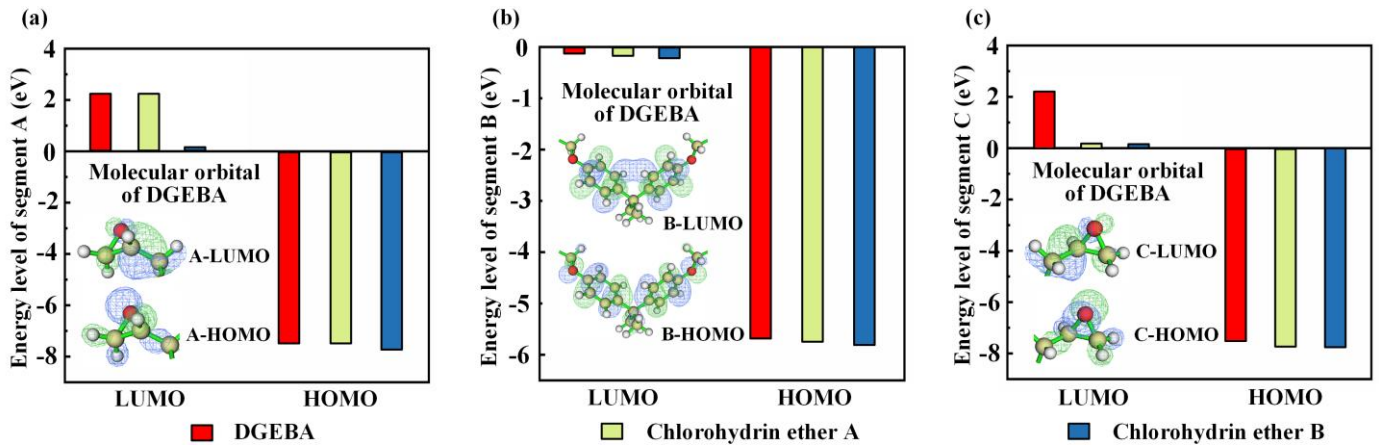


**Figure 4.** The energy band structure and distributed energy levels of chlorohydrin ether B molecule.

The electron trap depth  $\phi_{te}$  of chlorohydrin ether A molecule in Fig. 3 is 0.364 eV (the difference between 0.199 eV and -0.165 eV), and the hole trap depth  $\phi_{th}$  is 1.795 eV (the difference between -5.723 eV and -7.518 eV). The electron trap depth  $\phi_{te}$  of chlorohydrin ether B molecule in Fig. 4 is 0.365 eV (the difference between 0.149 eV and -0.216 eV), and the hole trap depth  $\phi_{th}$  is 1.934 eV (the difference between -5.789 eV and -7.723 eV). Compared with those of DGEBA molecule, the electron trap depth of chlorohydrin ether A molecule and chlorohydrin ether B molecule decrease greatly, but the hole trap depth does not change significantly. The change of charge trap depth of the molecule is affected by the change of the distributed energy levels, so next we compare the distributed energy levels of above three kinds of molecules.

Fig. 5 shows the changes of LUMO and HOMO energy levels of segment A, segment B, and segment C of DGEBA, chlorohydrin ether A, and chlorohydrin ether B molecules. It can be seen from Fig. 5b that after the introduction of chlorine atom into the epoxy group segment, the LUMO and HOMO

energy levels of the adjacent segment of the epoxy group segment decrease slightly, and with the increase of the number of chlorine atoms introduced, the extent of the decrease of both LUMO and HOMO energy levels of this segment increase slightly. From the distributed energy levels of the molecules in Fig. 2, Fig. 3, and Fig. 4, it can be seen that compared with those of DGEBA molecule, the LUMO and HOMO energy levels of segment B of chlorohydrin ether A molecule introduced a chlorine atom decrease by 0.055 eV and 0.076 eV, respectively; compared with those of DGEBA molecule, the LUMO and HOMO energy levels of segment B of chlorohydrin ether B molecule introduced two chlorine atoms decrease by 0.106 eV and 0.142 eV, respectively. Fig. 5a and Fig. 5c show that after the introduction of chlorine atom into the epoxy group segment, the LUMO and HOMO energy levels of the interphase segment of the epoxy group segment almost have no change, but the LUMO and HOMO energy levels of the epoxy group segment change obviously. To be specific, the LUMO energy level of the epoxy group segment shows a significant decrease, and the HOMO energy level of the segment shows a smaller decrease.



**Figure 5.** The changes in LUMO and HOMO energy levels of different segments of DGEBA, chlorohydrin ether A, and chlorohydrin ether B molecules. (a): Segment A; (b): Segment B; (c): Segment C

For example, compared with those of DGEBA molecule, the LUMO energy level and homo energy level of segment C of chlorohydrin ether A molecule decrease by 2.025 eV and 0.211 eV, respectively.

#### D. Modulation Laws of the Chlorine

After the introduction of chlorine into epoxy group segment of DGEBA molecule, the LUMO energy level of the epoxy group segment shows a significant decrease, and the HOMO energy level of the segment shows a smaller decrease; the LUMO and HOMO energy levels of the adjacent segment of the epoxy group segment decrease slightly; the LUMO and HOMO energy levels of the interphase segment of the epoxy group segment almost have no change.

After the chlorine is introduced into epoxy group segment, the electron trap depth of the molecule decreases greatly, but the hole trap depth does not change obviously.

### III. ANALYSIS OF MODULATION LAWS

The effect induced by the electronegativity of chlorine is a kind of electrostatic interaction, which rapidly weakens and eventually disappears with the increase of carbon chain length. Therefore, the introduction of chlorine into the epoxy group segment has little effect on the energy levels of DGEBA internal segment, as described above. Then we analyze and explain the modulation laws of the chlorine introduced into epoxy group segment on energy levels of the epoxy group segment and its adjacent segment

#### A. Modulation on Energy Levels of Epoxy Group Segment

When an atom with strong electronegativity is introduced into a certain molecular segment, the atom will attract the orbital electrons in the segment, including the orbital electrons between and on the valence bonds. After the orbital electrons between the valence bonds are attracted, the electron cloud offsets towards the position of the electronegative atom, and the electron cloud density between the nucleus of electronegative atom and the nucleus of the atom whose orbital electrons have shifted increases, which makes the electron orbital system between the valence bonds more stable and the energy of the

system lower. Therefore, the LUMO energy level of the segment containing the electronegative atom decreases with the decrease of the energy of the orbital electrons (conduction band electrons) moving between the valence bonds. After the orbital electrons on valence bonds are attracted by the electronegative atom, the electron cloud on valence bonds offsets, the density of the electron cloud decreases, and the overlap of the electron cloud on the valence bond decreases, which makes the covalent bond formed between the bonding atoms more unstable and the energy of the valence bond system increase. Thus, after the introduction of electronegative atom into the molecular segment, the HOMO energy level of the segment increases with the increase of the energy of the orbital electrons moving on the valence bonds.

Compared with DGEBA molecule (Fig. 1a), the epoxy group in segment C of chlorohydrin ether A molecule (Fig. 1b) is ring-opened and a chlorine atom is connected to the methylene group after ring-opening. On the one hand, the strong electronegativity of chlorine atom makes the chlorine atom strongly attract the orbital electrons between valence bonds in segment C of chlorohydrin ether A molecule, which offsets the electron cloud between valence bonds towards the position of the chlorine atom. Therefore, the electron cloud density between chlorine nucleus and carbon nucleus in segment C increases, and the energy of electron orbital system between valence bonds in segment C decreases. On the other hand, after the introduction of the chlorine atom into the epoxy group, there is a repulsive interaction between the extranuclear electrons of the chlorine atom and the extranuclear electrons of the oxygen atom that was originally in the epoxy group. As a result of this repulsion, the average radius of motion of orbital electrons between valence bonds around the chlorine atom and the oxygen atom decreases, so the potential energy of the orbital electrons decreases, which reduces the energy of these orbital electrons between the valence bonds in segment C. Therefore, after introducing a chlorine atom into the epoxy group segment, the LUMO energy level of the segment will be greatly reduced.

The epoxy group in segment C of DGEBA molecule is a three-membered ring, in which the oxygen atom is connected with two carbon atoms. Due to the strong electronegativity of the oxygen atom, the orbital electrons on the two O-C polar

covalent bonds formed with oxygen atom shift towards the position of the oxygen atom. After opening the epoxy group and connecting a chlorine atom to the methylene group (Fig. 1b), the orbital electrons on the O-C polar covalent bond formed with oxygen atom in segment C shift towards the position of the oxygen atom, and the orbital electrons on the Cl-C polar covalent bond formed with chlorine atom shift towards the position of the chlorine atom. Since the electronegativity of chlorine atom (3.16, relative value) is less than that of oxygen atom (3.44, relative value), the polarity of the Cl-C covalent bond is weaker than that of the O-C covalent bond, which makes the offset degree of the orbital electrons on the Cl-C covalent bond smaller than that of the O-C covalent bond. Therefore, after introducing a chlorine atom into the epoxy group segment of DGEBA molecule, the offset degree of the orbital electrons on valence bonds in the epoxy group segment becomes smaller, which makes the valence bond system in the segment more stable and the HOMO energy level of the segment shows a small decrease.

It can be seen from the distributed energy levels in Fig. 2 and Fig. 4 that, compared with those of DGEBA molecule, the LUMO energy levels of segment A and segment C of chlorohydrin ether B molecule significantly decrease and the HOMO energy levels slightly decrease. These features are also consistent with the above modulation analysis of the chlorine introduced in epoxy group segment on its molecular orbital energy levels.

### B. Modulation on Energy Levels of the Adjacent Segment

As mentioned above, compared with those of DGEBA molecule, both the LUMO and HOMO energy levels of segment B of the chlorohydrin ether A molecule slightly decrease, but the distribution of their corresponding molecular orbitals does not change. It can be seen from Fig. 2c-1 and Fig. 2c-2 that the molecular orbital corresponding to the LUMO energy level of segment B of DGEBA molecule is concentrated on the benzene rings, and the molecular orbital corresponding to the HOMO energy level is concentrated on the benzene rings and the ether oxygen groups connected to them. In the DGEBA molecule, the 2p orbitals of the oxygen atoms in ether oxygen groups connected to the benzene rings form p- $\pi$  conjugation with the large  $\pi$  orbitals of the benzene rings, which makes the density of electron cloud between conjugate atoms in the conjugated system decrease and the internal energy of the system decrease. Therefore, the conjugated system formed is relatively stable.

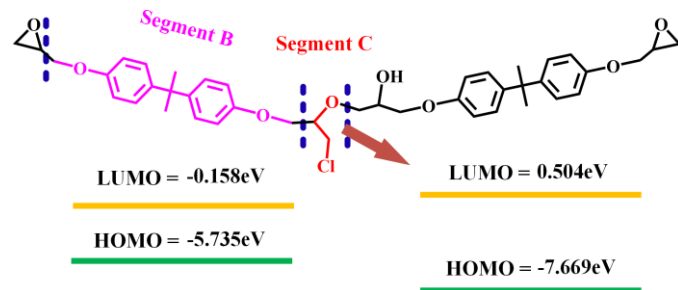
As shown in Fig. 2a, in the optimized DGEBA molecule, the C-C-O bond angle formed by the two carbon atoms connecting segment B and segment C and the oxygen atom in the epoxy group segment is  $114.83^\circ$ . After opening the ring of the epoxy group and connecting the chlorine atom to the methylene group after the ring-opening (shown in Fig. 3a), the C-C-O bond angle decreases to  $105.32^\circ$ , which indicates that the oxygen atom in epoxy group segment has shifted towards the segment B. As a result of this shift, the 2p orbital of the oxygen atom in epoxy group segment is slightly conjugated with the large  $\pi$  orbitals of

the benzene rings in segment B, which results in a slight decrease in the electron cloud density of the original conjugated system in segment B and makes the conjugated system more stable. In this way, compared with that of DGEBA molecule, the energy of the conjugated system in segment B of chlorohydrin ether A molecule is slightly lower, and the HOMO energy level of segment B is also slightly lower. At the same time, after the oxygen atom in epoxy group segment shifts towards segment B, the extranuclear electrons of the oxygen atom repulse with the  $\pi^*$  electrons in segment B. As a result, the average motion radius of the orbital electrons moving around the orbital center in the antibonding orbital is slightly smaller, and the energy of electrons in the antibonding orbital is slightly reduced. Therefore, compared with that of DGEBA molecule, the LUMO energy level of segment B of chlorohydrin ether A molecule slightly decreases.

Compared with DGEBA molecule, the epoxy groups in segment A and segment C of chlorohydrin ether B molecule (Fig. 4a) are both opened and introduced with a chlorine atom, so the energy levels of the segment B will be affected by the structural changes of both segment A and segment C. Therefore, compared with that of chlorohydrin ether A molecule with a chlorine atom introduced, the decrease extent of LUMO and HOMO energy levels of segment B of chlorohydrin ether B molecule with two chlorine atoms introduced both have a slight increase, as shown in Fig. 5.

### C. Effect of Non-Hydrolyzable Chlorine Atom on Energy Levels Distribution

As shown in Fig. 1b, the hydroxyl group and chloromethyl group are connected to the carbon atom in the methine group in segment C. The chlorine atom in the chloromethyl group is easily hydrolyzed, which makes it difficult to exist stably in the chlorohydrin ether A molecule. The hydroxyl group in chlorohydrin ether A molecule can react with the epoxy group in DGEBA molecule to form an ether bond, as shown in Fig. 6. In this way, the chlorine atom in segment C exists in isolated chloromethyl group, which turns the hydrolyzable chlorine atom into the non-hydrolyzable chlorine atom to exist stably in the molecule generated after the reaction.



**Figure 6.** The distributed energy levels of the molecule containing the non-hydrolyzable chlorine atom.

The distributed energy levels and charge trap depth of the molecule containing the non-hydrolyzable chlorine atom and the chlorohydrin ether A molecule were compared, in order to explore whether the modulation laws of chlorine changed after the hydrolyzable chlorine atom was turned into non-hydrolyzable chlorine atom.

Using the same calculation method as above, we obtained the distributed energy levels of the molecule containing nonhydrolyzable chlorine atom, as shown in Fig. 6. Comparing the LUMO and HOMO energy levels of segment B and segment C of the molecule in Fig. 6 and the chlorohydrin A molecule in Fig. 3, we can see that the energy levels have no obvious changes except for a slight increase in the LUMO energy level of segment C of the molecule in Fig. 6. The increase of the LUMO energy level is attributed to the weakening of the inductive effect of chlorine on the orbital electrons between the valence bonds in segment C due to the change of the position of chlorine atom. The electron trap depth and hole trap depth between segment B and segment C in Fig. 6 are 0.662eV and 1.934eV, respectively. Compared with the charge trap depth of chlorohydrin A molecule in Fig. 3, the charge trap depth between segment B and segment C of the molecule in Fig. 6 does not change significantly.

The comparisons of above distributed energy levels and charge trap depth show that, the transformation of hydrolysable chlorine atom into non-hydrolyzable chlorine atom does not affect the modulation laws of chlorine introduced into epoxy group segment on distributed energy levels and charge trap depth of the molecule.

#### IV. EFFECT ON THE CHARGE TRANSPORT

The chlorine introduced into the epoxy group segment changes the energy levels of the molecular chain segments, and it is the changes of the energy levels of these segments that affect the charge trap depth of the molecule. It can be seen from the above that the introduction of chlorine into the epoxy group segment greatly decreases the electron trap depth, but does not significantly change the hole trap depth of the molecule. The great decrease in the depth of the electron trap affects the transport of electrons along the molecular chain.

We introduced two electrons into the DGEBA molecule and the chlorohydrin ether B molecule, respectively. Recalculating the charge distribution of these molecules using DFT with Gaussian 09 software, we obtained the Mulliken atomic charges (the effective electric charge distribution of protons and orbital electrons) and their coordinates (standard orientation). Two spheres with the same radius (the sphere radius is selected to ensure that the sphere covers the segment C of the two molecules) are taken at the same position in the space regions of the DGEBA molecule and the chlorohydrin ether B molecule, as shown in Fig. 7. The surface electrostatic potential of the sphere is obtained using (1) and (2) [19], and displayed by a three-dimensional electrostatic potential diagram.

$$V(x, y, z) = \sum \Delta V(x, y, z) \quad (1)$$

$$\Delta V(x, y, z) = \frac{\Delta q(a, b, c)}{4\pi\epsilon_r\epsilon_0\sqrt{(a-x)^2 + (b-y)^2 + (c-z)^2}} \quad (2)$$

where  $V(x, y, z)$  is the total electrostatic potential,  $\Delta V(x, y, z)$  is the individual potential generated by the positive charges of protons and the negative charges of orbital electrons,  $\epsilon_r$  is the relative permittivity and  $\epsilon_0$  is the vacuum permittivity.

In Fig. 7, the surface of the sphere covering segment C of DGEBA molecule is concentrated in red, and the surface of the

sphere covering segment C of the chlorohydrin B molecule is alternately distributed in yellow, green and blue. The comparison of the two spherical surface electrostatic potential shows that, the negative charges on segment C of chlorohydrin ether B molecule increase compared with that of DGEBA molecule after introducing the electrons, which indicates that the electrons captured by chlorohydrin ether B molecule are easier to transfer from the electron trap site (the LUMO energy level of segment B) to segment C of the molecule. The similar migration processes whereby the extra electrons in chlorohydrin ether A and chlorohydrin B molecules are excited to easily escape from the shallow electron traps are marked in Fig. 3c and Fig. 4c, respectively.

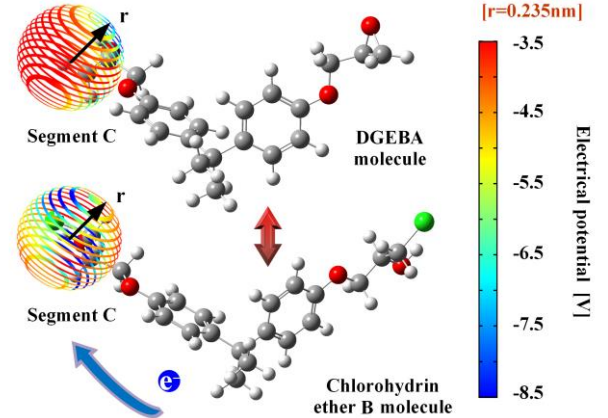


Figure 7. The electrostatic potential diagram of spherical surface.

The electron trap depth of the molecule affects the hopping probability of electrons, thus affecting the electron mobility in the transport process and the electrical conductivity of the material. Their relationships are shown in (3), (4) and (5), where  $\theta_{\text{hop}}$  is hopping probability,  $\phi_t$  is charge trap depth,  $k$  is Boltzmann constant,  $T$  is absolute temperature,  $\mu$  is carrier mobility,  $\mu_0$  is intrinsic mobility,  $\sigma$  is electrical conductivity,  $n$  is electron concentration,  $q$  is electron charge quantity,  $p$  is hole concentration [12, 16].

$$\theta_{\text{hop}} = \exp(-\phi_t / kT) \quad (3)$$

$$\mu = \mu_0 \theta_{\text{hop}} \quad (4)$$

$$\sigma = nq\mu_n + pq\mu_p \quad (5)$$

With the introduction of chlorine into the epoxy group segment of DGEBA molecule, the electron trap becomes shallower. It can be seen from (3) and (4) that the hopping probability of the electrons is higher, resulting in a higher electron mobility  $\mu_n$ . However, the introduction of the chlorine does not cause a significant change in the hole trap depth, so the hole mobility  $\mu_p$  does not change obviously. According to (5), the chlorine introduced into the epoxy group segment of DGEBA molecule increases the electrical conductivity of the polymer composed of the molecule.

The band gap width of DGEBA molecule in Fig. 2b is 5.537eV, that of chlorohydrin ether A molecule in Fig. 3b is 5.558eV, and that of chlorohydrin ether B molecule in Fig. 4b is 5.573eV. It can be seen that the band gap width of the molecule almost unchanged after the introduction of chlorine into the epoxy group segment. The band gap width represents the energy required for electrons to escape from valence bonds



and the barrier of electron migration between different lattices, which determines the intrinsic dielectric strength of the material. Therefore, after the chlorine is introduced into the epoxy group segment, the intrinsic dielectric strength of the material will not change significantly. To sum up, the introduction of chlorine into the epoxy group segment of the epoxy resin can improve the surface conductivity without affecting the intrinsic dielectric strength of epoxy materials.

## V. CONCLUSION

We found and explained the modulation laws of the chlorine introduced into the epoxy group segment of epoxy resin on molecular orbital energy levels and charge trap depth. Through its inductive effect and the effect of its introduction on the conjugation effect of oxygen atoms, the chlorine introduced can modulate the distribution density of orbital electrons between and on valence bonds, and then modulates the LUMO and HOMO energy levels of different molecular segments. It is the changes of the energy levels of these different segments that make the electron trap depth greatly decrease and the hole trap depth of the molecule insignificantly change, thus improving the surface conductivity of the epoxy materials.

In the above work, we have only considered the influence of intra-chain charge transfer on conduction, but there is also inter-chain charge transfer that can contribute to the conduction. The inter-chain trap site is a factor worth considering, and its formation may be related to the physical defect caused by the interaction of inter-chain atoms. However, the inter-chain trap site seems difficult to predict and modulate, which will be given more consideration in future work.

## ACKNOWLEDGMENT

The authors would like to thank the Science and Technology Project of SGCC under the project ID: 5500-202058406A-0-0-00.

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