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Mechanisms on electrical breakdown strength increment of polyethylene by aromatic carbonyl compounds addition: a theoretical study

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Abstract A theoretical investigation is accomplished on the mechanisms of electrical breakdown strength increment of polyethylene at the atomic and molecular levels. It is found that the addition of aromatic carbonyl compounds as voltage stabilizers is one of the important factors for increasing electrical breakdown strength of polyethylene, as the additives can trap hot electrons, obtain energy of hot electrons, and transform the aliphatic cation to relatively stable aromatic cation to prevent the degradation of the polyethylene matrix. The HOMO-LUMO energy gaps (E_g), the ionization potentials (IPs), and electron affinities (EAs) at the ground states of a series of aromatic carbonyl compounds are obtained at the B3LYP/6-311+G(d,p) level. The theoretical results are in good agreement with the available experimental findings, show that 2,4-dioctyloxybenzophenone (Bzo) and 4,4'-didodecyloxybenzil (Bd) molecules can effectively increase the electrical breakdown strength when they are doped into polyethylene because of their much smaller E_g values than all the other studied aromatic carbonyl molecules and excellent compatibility with polymers matrix.

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Introduction

Electron avalanche is one of the main electrical degradation mechanisms in cross-linking polyethylene (XLPE) insulated high-voltage cable at highly divergent electric fields. The degradation of dielectric material is caused by partial discharges and treeing breakdown [1]. If electrical treeing is initiated, it can cause dielectric breakdown as soon as an electrical tree channel has bridged [2, 3]. One way of improving their insulating abilities is the addition of certain organic molecules as voltage stabilizers [4–9], such as polycyclic aromatic compounds or benzophenone-like structures compounds. These reports show that the additives are believed to capture high energy electrons, dissipate their energy, and finally prevent the degradation of the polymer matrix. These high energy electrons, also named as "hot electrons", will impact with the voltage stabilizer molecules, and cause ionization of the stabilizer to produce a stable radical cation and release non-harmful electrons of lower energy. The voltage stabilizer can possibly be regenerated by combining with a free electron, which is suggested by Ashcraft and co-workers [4] who found a correlation between the voltage stabilizer efficiency and ionization energy of the stabilizer. Yamano and Endoh [5] reported that the azocompounds which contain electron-acceptor group are effective for increasing the breakdown strength when they

are added to low density polyethylene films. It was concluded that the reduction in the current is due to the trapping effect and the excitation effect of the additives with electron-accepting group. Subsequently, Yamano [6] investigated the roles of aromatic compounds of acene series as additive in increasing the breakdown strength of the film. Breakdown strength with 9-nitroanthracene was the highest among the films, and it was approximately 1.65 times higher than that without an additive. They advised that breakdown of the low density polyethylene film in the study undergoes the electron avalanche mechanism. Additives play a role in disturbing the generation of the avalanche, so the breakdown strength increases. The trapping effect, i.e., additive may trap the electron carrier, was considered to be the first factor. And the second factor is the excitation effect, i.e., the excitation of the additive may occur at the collision with the electron. The trap level and excitation energy are influenced by the electron donating/accepting tendency of the group connected to the benzene ring of the additive. The additives with an electron-accepting are more deeply trapped in the electron carrier than those with an electron-donating group. Yamano , Englund , and their co-workers [7, 8] reported that the addition of polycyclic aromatic hydrocarbons is effective for inhibiting the polymer molecule chain fracture caused by electron bombardment, thus increasing the initial voltage of electrical tree of polyethylene (PE) and inhibiting the electrical tree initiation. In 2012, a benzil type compound was evaluated as voltage stabilizer in a superclean XLPE by Jarvid and co-workers [9]. It shows that the investigated voltage stabilizer raises the electrical tree inception level significantly. Our research group observed that addition of acetophenone in the proper amount leads to a 50 % increase of the alternate current (AC) breakdown strength of XLPE.

Acetophenone is prototypical aromatic carbonyl compound. The sensitized phosphorescence excitation spectra of jet-cooled acetophenone have been measured by Ito M. and co-workers [10]. The lowest excited singlet state is S_1 (n, π^*) with the origin of S_1 (n, π^*) ← S_0 transition of 27 279 cm^{-1} (77.99 kcal mol^{-1}). The excitation energy is lower than the C-C bond breaking energy of 82.95 kcal mol^{-1}. The origin of the first triplet state T_1 (n, π^*) shows at 25 791 cm^{-1} (73.74 kcal mol^{-1}), and the triplet state T_2 (π, π^*) is suggested to lie near T_1 (n, π^*). Acetophenone are very weakly fluorescent, but highly phosphorescent under isolated molecular condition. This phenomenon has been explained theoretically by Fang and co-workers [11, 12] based on the discovery of the minimum energy crossing point among the three potential energy surfaces (S_1, T_1, and T_2) of acetophenone. The $S_1 \rightarrow T_1$ intersystem crossing through the $S_1/T_2/T_1$ three-state intersection can occur with a high rate.

These conjectural mechanisms are essential to understand the molecular functioning as voltage stabilizers in XLPE

composites against degradation of the polymer matrix. To the best of our knowledge, no previous theoretical work has been performed on the mechanism of electrical breakdown strength increment for polyethylene at the atomic and molecular levels. This work aims to provide a systematic study on the mechanism of electrical breakdown strength increment for XLPE when aromatic carbonyl molecules are adulterated. A comparison between the theoretical and experimental results is presented. Through our theoretical study, the behavior of aromatic carbonyl molecules for XLPE composite materials will be revealed, and a fertile theoretical background for the rational molecular design and synthesis of the desired voltage stabilizers in real applications will be provided. The research results will be helpful for further experimental investigations.

Computational methods

In the present work, the equilibrium geometries of all the stationary points of the neutral and ion states of the 46 studied molecules at the ground state are fully optimized using B3LYP [13–16] functional with the 6-311+G(d,p) basis set. Calculated harmonic vibrational frequencies are confirmed by normal-mode analysis to have real frequency corresponding to all of the vibrating modes. On the basis of these calculations, the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO) energy gaps (E_g), the ionization potentials (IPs), and the electron affinities (EAs) are obtained. In order to obtain more accurate energies of several key molecules, the energies of the equilibrium geometries are refined by the quadratic configuration interaction with single and double substitutions with a triple contribution QCISD(T) [17] method based on the B3LYP/6-311+G(d,p) geometries at ground state S_0 and the lowest triplet state T_1. All the electronic structure calculations are performed using GAUSSIAN09 program package [18]. The relevant schematic formulae can be defined as follows:

$$IP(\nu) = E^+(M) - E(M) \approx -E_{HOMO}$$
$$IP(a) = E^+(M^+) - E(M)$$
$$EA(\nu) = E(M) - E^-(M) \approx -E_{LUMO}$$
$$EA(a) = E(M) - E^-(M^-)$$

where $E^+(M^+)$, $E^-(M^-)$, and $E(M)$ represents the energies of the cation, anion, and neutral species in their lowest energy geometries, respectively, while $E^+(M)$ and $E(M^+)$ represents the energies of cation and neutral species with the geometries of neutral and cation, respectively, $E^-(M)$ and $E(M^-)$ represents the energies of anion and neutral species with the geometries of neutral and anion, respectively, where ν and a represents vertical energy based on the geometry of the neutral

molecule and adiabatic energy from the optimized structure for both the neutral and charged molecule, respectively.

The different substituent groups, such as carbonyl, alkyl, phenyl, and heteroatom, have been chosen in the present study to evaluate the substituent group effect,

functional group effect, and electronic effect. The role of the additive in increasing the breakdown strength is discussed by focusing on these three effects. The name, chemical structure, and corresponding abbreviations of studied molecules are listed below:

Molecular naming	ab.	Molecular naming	ab.
3-methyl-2-pentanone	Ac4	(4-mercapto)-phenylethanone	Apsh
1-(9-anthracenyl)-ethanone	Ae	benzeneacetaldehyde	Ba
(4-acetylphenyl)phenylmethane	Am	4,4'-didodecyloxybenzil	Bd
anthracene	An	Benzene	Be
9,10-dibromoanthracene	Anbr	benzyl methyl ketone	Bk
acetophenone	Ap	bis(4-methylphenyl)- Methanone	Bm
2-anthracenylethanone	1Ap	Benzophenone	Bz
2-acetylphenanthrene	2Ap	2,4-dioctyloxybenzophenone	Bzo
3-Acetylphenanthrene	3Ap	1-[1,1'-biphenyl]-4-yl-ethanone	Et
(4-bromo)-phenylethanone	Apbr	1-Keto-1,2,3,4-tetra-hydrophenanthrene	Kp
(4-methyl)-phenylethanone	Apc	4-methyl-benzeneacetaldehyde	Mb
(4-sec-butyl)-phenylethanone	Apc4	10-methylanthracene-9-carboxaldehyde	Mc
(4-chloro)-phenylethanone	Apcl	(2-methoxyphenyl)phenyl-Methanone	Mm
(4-cyano)-phenylethanone	Apcn	(2-methylphenyl)phenyl-methanone	2Mp
(4-fluoro)-phenylethanone	Apf	(3-methylphenyl)phenyl-methanone	3Mp
(4-amino)-phenylethanone	Apnh2	(4-methylphenyl)phenyl-methanone	4Mp
(4-methylamino)-phenylethanone	Apnhc	naphthalene	Na
(4-nitryl)-phenylethanone	Apno2	1-(1-naphthalenyl)-ethanone	Ne
(4-butoxy)-phenylethanone	Apoc4	2-naphthyl methyl ketone	Nk
(4-hydroxyl)-phenylethanone	Apoh	sec-butylbenzene	Pc4
4-(4-methyl-phenyl)-phenylethanone	Appc	1,3-diphenyl-2-propanone	Pd
(4-biphenyl)- phenylethanone	Appp	n-hexane	Pe6
(4-methoxy)-phenylethanone	Apoc	β-phenylpropiophenone	Po

Results and discussion

Frontier MOs, IPs, and EAs

The optimized geometric structures of the 46 molecules at the neutral state under the B3LYP/6-311+G(d,p) level are presented in Fig. 1. To clarify the influence of different substituent effect (such as carbonyl, phenyl, alkyl, and heteroatom), functional group effect, and electronic effect on the HOMO-LUMO energy gaps (E_g), the n-hexane, 3-methyl-2-pentanone, and sec-butylbenzene molecules are taken as reference molecules, and the values of the vertical and adiabatic ionization potentials (IPs), and the electron affinities (EAs) calculated at the B3LYP/6-311+G(d,p) level are shown in Table 1, including corresponding experimental data [19] in brackets. The ability of accepting a hot electron is closely related to molecular HOMO and LUMO. The relative orderings of HOMO and LUMO energies provide a

reasonable qualitative indication of the ability of the electron being accepted. From Table 1, it can be seen that the alkyl, carbonyl, phenyl, and heteroatom groups are efficacious to decrease the energy gap of HOMO and LUMO. Introducing carbonyl and benzene ring into the molecule is propitious to electronic dissociation because their high HOMO energies and hence small ionization potentials in terms of Koopmans' theorem. It is favorable for electron to be accepted because their low LUMO energies and hence larger electron affinities energies. To understand the role of carbonyl and benzene ring in their HOMOs and LUMOs quantitatively, we select n-hexane, 3-methyl-2-pentanone, and sec-butylbenzene as reference molecules. The introduction of carbonyl and phenyl groups in Ac4, Apc4, and Apoc4 decrease E_g compared with Pe6, because their ability of π-electron delocalization is stronger than that of the σ-electron (Pe6). The results indicate that the contributions of carbonyl group are larger than those of benzene ring substituted in decreasing their LUMO
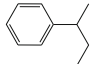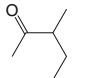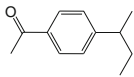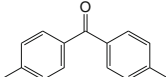
a

Ap	Bk	Apc	Ba	Mb	Apcn	Apnh2	Apnhc	Apno2	Be

Apoh	Apoc	Apsh	Apf	Apcl	Apbr	An	Apc4	Ac4	Pe6

Pd	3Mp	2Mp	Mc	Na

b

Appc	4Mp	2Ap	3Ap	Ne

Appp	Et	Bz	Nk	Pc4

Am	1Ap	

Bd	Apoc4	Anbr	Bzo

Bm	Po	Mm	Ae	Kp
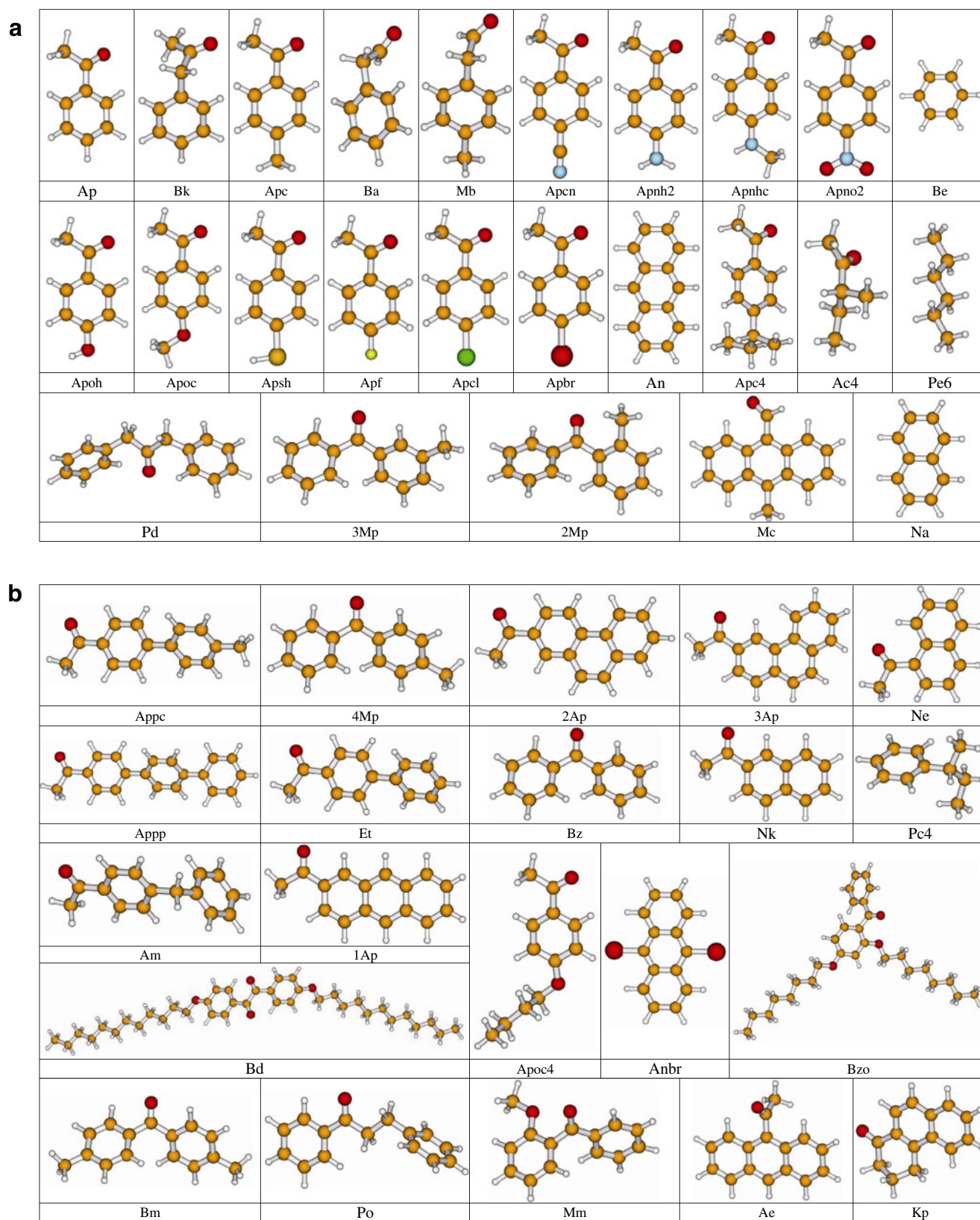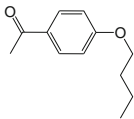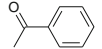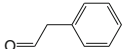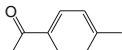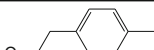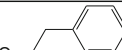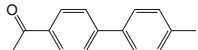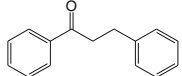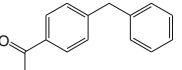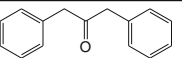
Fig. 1 Optimized geometric structures of the studied 46 molecules at the neutral state under the B3LYP/6-311+G(d,p) level

energies and E_g values. For the analysis of conjugated effect, those isomeric compounds are divided to three teams, Ap and Ba molecules as the first team, Apc, Mb, and Bk molecules as the second team, and Appc, Bm, Po, Am, and Pd molecules as

Table 1 The HOMO-LUMO energy gaps E_g, adiabatic ionization potentials IP(a), vertical ionization potentials IP(v), adiabatic electronic affinities EA(a), vertical electronic affinities EA(v) of studied molecules (in eV) calculated at the B3LYP/6-311+G(d,p) level as well as corresponding experimental data in brackets

ab.	molecular formula	E_g	IP(a)	IP(v)	EA(a)	EA(v)
Pe6	(structure)	8.76	9.76 (9.97)	10.80	-1.20	-0.23
Pc4	(structure)	6.32	8.48	8.66	-0.92	0.43
Ac4	(structure)	6.16	9.00	9.18	-0.71	0.71
Apc4	(structure)	5.22	8.55	8.77	0.30	1.79
Apoc4	(structure)	4.92	8.18	8.27	0.17	1.58
Ap	(structure)	5.20	8.95 (9.10 ± 0.10)	9.19	0.33 (0.33)	1.93
Ba	(structure)	5.70	8.79 (9.30 ± 0.10)	8.86	-0.25	1.37
Apc	(structure)	5.22	8.66 (8.85)	8.91	0.25	1.80
Mb	(structure)	5.55	8.46	8.55	-0.28	1.30
Bk	(structure)	5.73	8.52 (8.98)	8.59	-0.37	1.12
Appc	(structure)	4.54	7.94	8.02	0.75	2.03
Bm	(structure)	4.93	8.29	8.33	0.61	1.95
Po	(structure)	4.89	8.35	8.37	0.49	1.96
Am	(structure)	5.03	8.35	8.38	0.42	1.84
Pd	(structure)	5.87	8.11 (8.50 ± 0.10)	8.12	-0.17	0.88

the third team. The molecules with the conjugative effect have smaller value of E_g than that without it, for instance E_g (Ap) < E_g (Ba), E_g (Apc) < E_g (Mb and Bk), etc. The degree of coplanarity between benzene ring and carbonyl will affect the corresponding E_g. For Bm, as the two benzene rings link to a carbonyl directly, the steric hindrance is big, it causes the two benzene rings to not be planar, the degree of Bm coplanarity is smaller than Appc, so that the value E_g of Bm is larger than that of Appc. For benzene ring, due to π-electron delocalization and the conjugated of π-π (Ap), σ-π (Apc), p-π (Apoc4), E_g evidently decreases.

The ionization potentials (IPs) and the electron affinities energies (EAs) of the molecules are the most important parameters to characterize the reduction and oxidation ability, respectively. Thus, IP and EA values are calculated, as listed in Table 1. From Table 1, it can be seen that these conjugated aromatic ketone molecules (Ap, Apc, Apoc4, Apc4, Appc, and Bm) with carbonyl and benzene ring possess larger EA(v) (1.58-2.03 eV) than that of Pe6 (−0.23 eV) and smaller IP(v) (8.01–9.19 eV) values than that of Pe6 (10.80 eV) due to their low LUMO and high HOMO energy levels. Their large EA(v) values give rise to high stability of the anions. Their small

IP(v) values probably enhance the stability of the cations. Thus, these conjugated aromatic ketone molecules possess strong capability of trapping electrons and releasing electrons. In other words, for aromatic carbonyl molecules, the larger the electron affinities are, the more easily hot electrons are trapped; the smaller ionization potentials are, the more easily electrons are released. As we expected, they possess low barriers of electrons being accepted because of their low LUMO energy levels. Through the discussion above, the introduction of carbonyl and benzene ring largely improves the accepted ability of these molecules for electrons. To further demonstrate phenyl substituent effect and conjugated effect, benzene rings stacking and linking, and different conjugated types (such as π-π, σ-π, p-π) for the molecules with carbonyl and benzene rings will be discussed in detail in the following section.

Energies: molecular stacking and linking
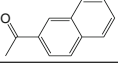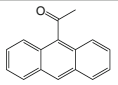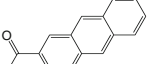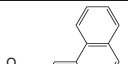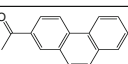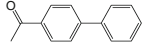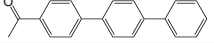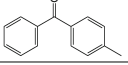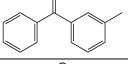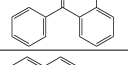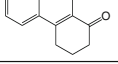
The substituent functional groups, the amount of benzene rings, stacking and linking motifs have influence on their frontier molecular orbitals of the studied aromatic carbonyl molecules. These acene, lemonene, benzophenone-like compounds are studied. The corresponding E_g, IPs, and EAs of the molecules calculated at the B3LYP/6-311+G(d,p) level are listed in Table 2 as well as corresponding experimental data [19]. The results show that the E_g of the studied polycyclic aroma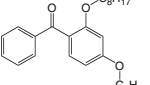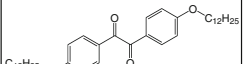tic compounds are lower than that of monocyclic aromatic compounds. For example, E_g (Na, An and Anbr) < E_g (Be), E_g (Nk, Ne, Ae, Mc, 1Ap, 2Ap and 3Ap) < E_g (Ac). The aromaticity of the studied polycyclic aromatic compounds is lower than that of monocyclic aromatic compounds, and the ability of π-electron delocalization is stronger when aromaticity decreases. From Table 2, it is shown that the relative orientations of substituent functional groups have little effect on the HOMO-LUMO energy gap. For example, E_g of Nk (4.29 eV) is larger than that of Ne (4.25 eV). E_g is larger when substituent functional group is linked to the active site, e.g., E_g of Nk and Ae molecules is larger than that of Ne and 1Ap molecules. With increasing of number of benzene rings, E_g decreases, such as Be, Na, and An; Ac, NK, and 1Ap; Ac, Et, and Appp. From Table 2, it is also shown that the molecules with stronger aromaticity usually have larger E_g values, such as Et vs Nk, Appp vs 1Ap, because the aromaticity of Et and Appp is stronger than Nk and 1Ap, respectively. For isomeric compounds Et, 4Mp, 3Mp, and 2Mp, the HOMO-LUMO gaps E_g of 4Mp, 3Mp, and 2Mp are larger than that of Et. The main factor is that the non coplanarity dihedral angel of the two benzene rings (2Mp is 60°) is larger than that of Et (40°), so it does not provide optimal π-orbital overlap, and their conjugated character decreases. For Bzo and Bd molecules, Bd possesses p-π-π-π-π-p conjugated effect, more

importantly, two benzene rings link with difference carbonyl. Therefore, steric hindrance decreases evidently, the degree of coplanarity increases, and good conjugated effect is obtained. In a word, Bd possesses lower LUMO level than Bzo and hence better electron trapping ability. The energy of electronic transition is smaller when the molecular HOMO-LUMO energy gap (E_g) decreases. As the result, for benzophenone-like molecules, with increasing of number of heteroatom (O atom) and alkyl, E_g decreases significantly. The calculated results explained well the reports by Jarvid , Englund , and their co-workers [8, 9] that the introduction carbonyl and alkoxy into benzophenone molecules is an exciting molecular design because they can effectively decrease E_g value and possess excellent compatibility with polymers matrix, e.g., E_g of Bzo (4.44 eV) and Bd (4.22 eV) are smaller than that of Bz (4.90 eV). At the same time, E_g of Mm (4.50 eV) is smaller than that of Bz too. The substitutions by carbonyl and heteroatom groups lead to the reduction of the corresponding energy margin of HOMO and LUMO.

Energies: electronic effect

In order to further evaluate electronic effect of aromatic ketone with para-position substituent group, three conjugated types are compartmentalized, π-π (Apcn, Apno2, and Et), σ-π (Apc), and p-π (Apf, Apcl, Apbr, Apoc, Apnh2, Apnhc, Apoh, and Apsh). Calculated values at the B3LYP/6-311+G(d,p) level including E_g, IPs, and EAs of the studied molecules are listed in Table 3, together with the available experimental data [19]. As discussed above, conjugated effect can efficiently reduce E_g value. The alkyl groups linked to benzene ring in Apc will exhibit inductive electron-donating effect and σ-π super-conjugated effect weakly, E_g (Apc) and E_g (Ap) are close to each other. When the alkyl group of Apc was replaced by –CN, –NO$_2$, or –Ph groups with π-bond, E_g decreases because of the π-π-π conjugated effect, e.g., E_g (Apcn, Apno2, and Et)<E_g (Ap). When the alkyl group of Apc was replaced by halogen, O, N, and S, the π-π-p conjugated effect are formed, so E_g of Apf, Apcl, Apbr, Apoc, Apnh2, Apnhc, Apoh and Apsh is lower than that of Ap. As the heteroatom electronegativity follows the order of F > O > Cl > Br ~ N > S, the E_g in Table 3 follows the order of Apf> Apcl > Apoh > Apbr > Apnh2 ~ Apsh. As is well-known, the N and O atoms have smaller electronegativity than F and Cl atoms as well as close atomic radius to C, so electron-donating effect in Apoh and Apnh2 is stronger than Apf and Apcl, the electronic density of benzene ring in Apoh and Apnh2 is larger than Apf and Apcl. As a result, the E_g values tend to be smaller from Apcl to Apoh, and Apbr to Apnh2. Electron density in benzene will decrease when the para-positon of acetophoene is linked with halogen atoms (F and Cl), due to the fact that halogen atoms are deactivating groups. The decreased electron density will increase the corresponding

Table 2 The E_g, IPs, and EAs of studied molecules (in eV) calculated at the B3LYP/6-311+G(d,p) level as well as the corresponding experimental data in brackets

	Molecular formula	E_g	IP(a)	IP(v)	EA(a)	EA(v)
Ap		5.20	8.95 (9.10 ± 0.10)	9.19	0.33 (0.33)	1.93
Be		6.60	9.13 (9.24)	9.28	-1.16	0.48
Na		4.75	7.88 (8.14)	7.97	-0.199 (-0.20)	1.40
An		3.55	7.09	7.16	0.59	2.02
Anbr		3.33	7.25 (7.58)	7.33	1.21	2.54
Nk		4.29	8.02 (8.31)	8.14	0.69	2.12
Ne		4.25	8.00 (8.23)	8.13	0.79 (0.60 ± 0.03)	2.24
Ae		3.49	7.19	7.28	1.14 (1.02 ± 0.10)	2.26
Mc		3.15	7.26	7.37	1.39	2.71
1Ap		3.34	7.24	7.33	1.16	2.47
3Ap		4.16	7.73	7.85	0.84	2.15
2Ap		4.27	7.77	7.90	0.83	2.16
Et		4.62	8.06	8.26	0.79	2.07
Appp		4.22	7.50	7.71	1.03	2.12
4Mp		4.87	8.28 (9.13 ± 0.05)	8.49	0.67	2.01
3Mp		4.977	8.34	8.57	0.70	2.075
2Mp		4.96	8.37	8.55	0.67	2.068
Kp		4.31	7.89	8.01	0.67	2.05
Bz		4.90	8.64	8.67	0.73	2.10
Mm		4.50	7.88	8.13	0.51	1.90
Bzo		4.44	7.31	7.66	0.40	1.67
Bd		4.22	7.60	7.77	1.28	2.15

Table 3 The E_g, IPs, and EAs of studied molecules (in eV) calculated at the B3LYP/6-311+G(d,p) level as well as corresponding experimental data in brackets

	Molecular formula	E_g	IP(a)	IP(v)	EA(a)	EA(v)
Ap	(acetophenone)	5.20	8.95 (9.10 ± 0.10)	9.19	0.33 (0.33)	1.93
Apcn	(–CN)	5.16	9.35	9.57	1.29	2.15
Apno2	(–NO$_2$)	4.33	9.53	9.79	1.90	3.38
Apf	(–F)	5.26	9.01	9.28	0.41	2.01
Apcl	(–Cl)	5.22	8.89	9.21	0.60	1.80
Apbr	(–Br)	5.03	8.82	9.08	0.65	2.18
Apoc	(–O–)	4.98	8.25	8.47	0.11	1.63
Apnh2	(–NH$_2$)	4.75	7.79	8.05	-0.010	1.49
Apnhc	(–NH–)	4.57	7.51	7.66	-0.008	1.38
Apoh	(–OH)	5.14	8.48	8.74	0.14	1.73
Apsh	(–SH)	4.66	8.29	8.43	0.62	1.98
Apc	(–CH$_3$)	5.22	8.66 (8.85)	8.91	0.25	1.80
Et	(biphenyl ketone)	4.62	8.06	8.26	0.79	2.07

E_g, as a result, E_g(Apf) and E_g(Apcl) are bigger than E_g(Ap). Distinct electron-donating conjugated effect and relatively weak electron-withdrawing effect is present when N and O are linked to benzene ring (Apoh, Apoc, Apnh2, and Apnhc). The combined result is that E_g evidently decreases for acetopheone with the –OH, –OMe, –NH$_2$, and –NHMe at the para-position, so as E_g (Mm, Bzo and Bd) < E_g (Bz) (see Table 2). From Table 3, when –OH and –NH$_2$ are replaced by –OMe and –NHMe, respectively, the better electron-donating ability of alkyl group arouses electron density to increase weakly, then E_g decreases, so E_g (Apoc) < E_g (Apoh) and E_g (Apnhc) < E_g (Apnh2).

Excitation energies

The relative energies in the excited singlet state (S$_1$) and T$_1$ states of Be, Na, An, and Ap calculated at the QCISD(T)/6-311+G(3df,2p)//B3LYP/6-311+G(d,p) levels with zero-point energy (ZPE) corrections are listed in Table 4 as well as the corresponding experimental data [10, 20–22]. The calculated energies ΔE^{T1-S0} are very close to the experimentally values, for instance, ΔE^{T1-S0} of acetophenone is 74.92 kcal mol^{-1} which shows good consistency with the experimentally result of 73.74 [10] kcal mol^{-1}. This implies that the calculated

single-point energies at QCISD(T)//B3LYP level and geometric structures at B3LYP/6-311+G(d,p) level are reasonable and reliable. It is known that the C-C bond breaking energy is about 82.95 kcal mol^{-1}. This means that if the excited energies of S$_1$ ← S$_0$ state of any molecules are larger than 82.95 kcal mol^{-1}, the electronic transition process is not competitive to the C-C bond breaking, and then those molecules cannot be used as voltage stabilizer adulterate to

Table 4 The calculated singlet–triplet energy gaps ΔE^{T1-S0} (in kcal mol^{-1}) at the QCISD(T)/6-311+G(3df,2p)//B3LYP/6-311+G(d,p) level with zero-point energy (ZPE) corrections, together with the experimental data of energy gaps ΔE^{S0-S1} and ΔE^{T1-S0}

	ΔE^{T1-S0}_{calc}	ΔE^{T1-S0}_{Expl}	ΔE^{S0-S1}_{Expl}
Be	85.35	84.63 (3.67 eV)[a]	112.99 (4.90 eV)[a]
Na	61.51	60.88 (2.64 eV)[b]	92.01 (3.99 eV)[b]
An	43.87	42.70 (1.85 eV)	79.10 (3.43 eV)[c]
Ap	74.92	73.74[d]	77.99[d]

[a] Ref.[20]
[b] Ref.[21]
[c] Ref.[22]
[d] Ref.[10]

XLPE material. Among the four molecules above, only the excited energy $\Delta E^{\text{S0-S1}}$ of An, and Ap are both lower than 82.95 kcal mol^{-1}. Thus, in principle, they are effective as a voltage stabilizer for increasing the breakdown strength of insulating XLPE material. However, these small molecules possess weak compatibility with polymers matrix, and can be separated out of polymers matrix easily, so they are not promising as voltage stabilizer for insulating XLPE material. These theoretical results are supported by corresponding experimental conclusions [7].

Mechanism

The carriers (electrons) which gain enough kinetic energy under the electric field in insulating materials are known as hot electrons. Afterward, bound electrons are knocked free from atoms through the collisions with hot electrons and new carriers are created. If this process forms a chain reaction, the carrier concentration will increase sharply, which results in a loss of insulating properties of the material. We conjecture that the mechanisms of aromatic carbonyl molecules as additive in XLPE composite material are as follows, (1) the additive of aromatic carbonyl compounds with π-electron delocalization can trap hot electrons to form relatively stable anion radical; (2) the aromatic carbonyl compounds can obtain the energy from hot electrons through interaction to accomplish its electronic transition. Meanwhile, the interaction process with the additives can also decrease the kinetic energy of the hot electrons; (3) the additive of aromatic carbonyl compounds can transform the aliphatic cation to a relatively stable aromatic cation. For acetophenone (Ap), according to our conjectured mechanism, it can trap hot electrons due to possessing π-electron delocalization, the EA(v) value of Ap 1.93 eV is larger than that of Pe6 -0.23 eV, the ability of trapping electron is stronger with increasing of the electron affinities (EAs); Ap may obtain the energy of the hot electrons through the interaction with the hot electrons, and is initially excited to their S_1 states when the energy exceeds 77.99 kcal mol^{-1}. Rapidly, the $S_1 \rightarrow T_1$ intersystem crossing occurs effectively through the $S_1/T_2/T_1$ three-state intersection with a high electronic transfer rate. The highly phosphorescent but only weakly fluorescent occur simultaneity. The excitation may decrease the kinetic energy of the hot electron. The process occurs repeatedly. Consequently, Ap dissipate the hot electron energy and decrease the kinetic energy of the hot electron at the same time. Because aromatic cation possess strong ability of π-electron delocalization than that of aliphatic cation, Ap can also restore the aliphatic cation radical from transforming the aliphatic cation to relatively stable aromatic cation. With the macro-point of view, as a consequence, the insulating XLPE material exhibits an elevated AC breakdown strength. The addition of aromatic carbonyl compounds can prevent degradation of the polymer matrix.

The understanding of the mechanism of aromatic carbonyl compounds as a voltage stabilizer for increasing the breakdown strength of XLPE can provide the basis for our further design of an exciting voltage stabilizer with the improved XLPE electrical properties improvement. Our calculations may provide reliable information for future experiment investigations.

Conclusions

A systematically theoretical study on the mechanisms of aromatic carbonyl compounds as voltage stabilizers for increasing the breakdown strength of XLPE has been carried out. When the aromatic carbonyl compounds are doped to XLPE as voltage stabilizer, they, with the introduced carbonyl, phenyl, and alkoxy groups, can effectively improve electron-accept ability to trap the hot electron. Voltage stabilizers obtain the energies of hot electrons through interaction and dissipate them through electronic transition. As the energies of electronic transition of the additive is lower than that of C-C single bond breakdown in XLPE, the voltage stabilizer can prevent the hot electrons from hitting C-C bond of XLPE matrix. Voltage stabilizers can also restore aliphatic cation radical through transforming the aliphatic cation to relatively stable aromatic cation. The results imply that the introduction of carbonyl, phenyl, and alkoxy groups into benzophenone molecules is an exciting design of the molecules as voltage stabilizer.

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