Physics Letters A 381 (2017) 3732–3738

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

A study on ionization potential and electron trap of vegetable insulating oil related to streamer inception and propagation

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ARTICLE INFO

Article history:
Received 25 May 2017
Received in revised form 12 September 2017
Accepted 25 September 2017
Available online 28 September 2017
Communicated by F. Porcelli

Keywords:
Vegetable insulating oil
Streamer
Ionization potential
Electron affinity
Electron trap
Density functional theory

ABSTRACT

Vegetable oils, mainly composed of triacylglycerol molecules, have been widely studied as new insulation materials in the recent years. In this work, we study the electronic properties of various triacylglycerol molecules with different degree of unsaturation by density functional theory (DFT). The ionization potential (IP), electron affinity (EA), and electron trap are estimated by theoretical analysis and experiments. The results show that the C atoms of *cis* C=C double bond make the primary contribution to the highest occupied molecular orbital (HOMO) of unsaturated triacylglycerol molecule; the IPs of fully unsaturated triacylglycerol molecules are almost confined to the narrow ranges from 7.30 to 7.45 eV in gas-phase and from 6.77 to 6.84 eV in liquid-phase correspond to LnLnLn and OOO molecules, respectively; the atoms of ester group and neighboring atoms make the primary contribution to the lowest unoccupied molecular orbital (LUMO) of both saturated and unsaturated triacylglycerol molecules; the EAs of triacylglycerol molecules are confined to the narrow ranges from −0.34 to −0.18 eV and the chemical trap is estimated to be 0–0.16 eV; the total trap is 0.32–0.36 eV. The IP distribution character and shallow trap feature maybe the main causes that vegetable oils demonstrate a low resistance against the fast streamers. The work can provide theoretical basis to molecular modification for performance improvement of vegetable insulating oils.

1. Introduction

In recent years, vegetable oils have been studied extensively as alternative liquid dielectric for mineral oils in transformer and disconnector [1–8]. Vegetable oils mainly come from plant seeds such as soya, sunflower, rapeseed, cottonseed and olive. 21-days biodegradability of vegetable oils are up to 97%, superior to 30% for mineral oils. The environmental performance makes the material increasingly popular.

However, recent studies have shown that vegetable oils demonstrate a low resistance against the fast streamers (> 10 km/s) [4,9]. The streamer, commonly generated at sharp edges or at metallic protrusions, is a gas/plasma filled channel that incepts and propagates in the region under a high electric field. Streamers are divided into four modes according to their propagation rate, and modes 1–4 are roughly divided in the respective order of 100 m/s, 1 km/s, 10 km/s, and 100 km/s. Streamers propagate in the first mode at around the inception voltages, and propagate in the second mode at around the breakdown voltage. When the applied voltage increases over the breakdown voltage, the propagation velocity of streamers changes abruptly from the second to the third mode and, eventually, to the fourth mode at the so-called acceleration voltage. The modes 1–2 are called slow streamer and the modes 3–4 are called fast streamer. The propagation of streamer in vegetable oils tends to be faster and more branch-shaped than that in mineral oil. Especially, for vegetable oils, it is also interesting that fast streamers gradually becoming dominant in the long gap distance (≥ 50 mm).

Table 1 summaries the inception, breakdown and acceleration voltages respectively for vegetable insulating oil and mineral oil in a 50 mm gap from Ref. [5]. Although the inception voltage U_i of FR3 (nature ester insulating oil refined from soybean oil) and of Gemini X (mineral insulating oil) does not differ obviously, both the breakdown voltage U_b and acceleration voltage U_a for Gemini X are much higher than those values for FR3. Once the applied voltage on FR3 overs the U_a, the discharging is about to develop into fast streamer, which characterizes as the steamer velocity ramps from about 1 to 10 km/s. This has led to big difference between FR3 and Gemini X. Comparing with Gemini X, whose $U_a \gg U_b$, the U_a for FR3 almost equals its U_b.

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https://doi.org/10.1016/j.physleta.2017.09.037
0375-9601/

Table 1
Summary of inception, breakdown and acceleration voltage (kV).

Polarity	Positive			Negative		
Voltage	U_i	U_b	U_a	U_i	U_b	U_a
FR3	52.5	97.8	97.8	45.0	152.0	152.0
Gemini X	55.0	125.6	260.0	50.0	227.6	250.0

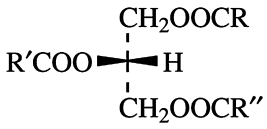

Fig. 1. Triacylglycerol molecule.

To date, considerable results have focused on the assessment of differences and similarities between vegetable oils and mineral oils based on experimental measurements and analysis. The main reasons why vegetable oils demonstrate a low resistance against the fast streamers are still not completely understood. There is a lack of investigation at the molecular level on diagnosing the influence of molecular type on streamer inception and propagation. It is well known that streamer is driven by a continuous liberation and capture of electrons in the process of propagation. The molecules comprising the dielectric are the sources of electrons and the energy is needed to ionize those molecules. The ionization potential (IP) will dominantly influence how far and how fast the streamers propagate. Furthermore, electron trap may capture of electrons and hinder the propagation, which originate from the electron affinity (EA) of molecules.

In this work, we study the electronic properties of various triacylglycerol molecules with different degree of unsaturation by density functional theory (DFT). The IP, EA, and electron trap are estimated by theoretical analysis and experiments. The effects of these properties on streamer inception and propagation are discussed. The calculations can increase our understanding of discharge properties of vegetable oils as a new insulation material and provide theoretical basis to molecular modification for performance improvement.

2. Methodology

2.1. Model and theoretical method

Triacylglycerol molecules account for more than 95% in vegetable insulating oil. A triacylglycerol molecule can be considered as one glycerol molecule esterified by three fatty acids. Fig. 1 is the structure of triacylglycerol molecule, in which R, R′, R″ represent fatty acids. The properties of triacylglycerol molecule are deeply affected by the fatty acids.

The fatty acids have chain lengths between C16 and C22, with C18 fatty acids dominating in most vegetable oils [10,11]. C18 fatty acids include stearic acid (S), oleic acid (O), linoleic (L), and α-linolenic (Ln). The models of four types of fatty acids are shown in Fig. 2. The four types of fatty acids can constitute 20 types of triacylglycerol molecules. They are SSS (0), SSO (1), SSL (2), SOO (2), SSLn (3), SOL (3), OOO (3), SOLn (4), SLL (4), OOL (4), SLLn (4), OOLn (4), OLL (5), SLnLn (6), OLLn (6), LLL (6), OLnLn (7), LLLn (7), LLnLn (8), and LnLnLn (9). The number of double bonds is marked in the brackets, standing for the degree of unsaturation of triacylglycerol molecules. The 20 types of triacylglycerol molecules are chosen to serve as representative molecules.

The IP and EA are two molecular parameters that have relation to the electric discharge in molecular liquids [12–14]. Koopman's theorem states that the ionization potential (IP) of a molecule is equal to the negative of the orbital energy of the highest occupied molecular orbital (HOMO), while the electron affinity (EA) is equal to the negative of the orbital energy of the lowest unoccupied molecular orbital (LUMO). The main assumption behind the theorem is the frozen orbital approximation, which is assumed that the molecular orbitals of the system are unmodified when adding or removing one electron. The calculations based on the theorem can only obtain qualitative results with obvious errors, especially for EA, compared with experimental data. At least, the theorem points out the relationship between the two molecular descriptors and the molecular orbitals. Hence, molecular orbital analysis are included in this work.

Our calculations are carried out using Gaussian 09 program package provided by Gaussian Inc [15]. The geometry of the triacylglycerol molecules are optimized using density functional theory (DFT) with Becke's three-parameter hybrid functional combined with the electron-correlation functional of Lee, Yang, and Parr (B3LYP) prescription employing the 6-31+G* basis set [16].

The IP is defined as the energy needed to remove an electron from neutral state A and create a positive ion A^+. An IP may equal the energy of the positive ion minus the energy of the neutral state of the ion. Geometric optimization of A is performed in order to evaluate the energy of the neutral molecule A. The energy of A^+ is calculated based on the optimized geometry of the neutral molecule. Hence, the IP, called the vertical IP in the gas phase, can be formulated as

$$IP = E^{A^+} - E^A. \tag{1}$$

The polarizable continuum model (PCM) has been used to calculate the IP [17]. In PCM, the surrounding liquid for a given molecule is treated as a continuum dielectric with a dielectric constant ε. It is set as 3.2 for triacylglycerol molecules to structure optimization [18]. The DFT method (B3LYP) with the 6-31+G* basis set is used as before. The definition of the IP in liquid phase can be modified as

$$IP = E^{A^+} - E^A + V_0, \tag{2}$$

where V_0 is the energy of a quasi-free electron in a condensed state. The values of V_0 are different in various dielectrics and there is no data available for vegetable oils, however, they are generally much less than the IP of the molecules (< 0.1 eV). Hence, the V_0 is neglected in this work [14,19].

As everyone knows, quantum chemical calculations of EA are more problematic compared to the calculation of the IP. Additionally, the value of EA is usually not big like IP and V_0 probably should not be neglected in the calculations of EA. Hence, the PCM is not implemented on EA. The EA is defined as the energy needed to remove an electron from a negatively charged ion A^-, written as

$$EA = E^A - E^{A^-}. \tag{3}$$

The difference value between the EAs of triacylglycerol molecules is defined as chemical trap related to molecular properties of triacylglycerol, written as [20]

$$E_{\text{trap}} = EA_i - EA_j, \tag{4}$$

where EA_i and EA_j are the value of EA of triacylglycerol molecules.

2.2. Experimental method

The thermally stimulated current (TSC) technique are used to measure the trap feature of electrons in dielectric [21]. The trap level can be calculated according to the TSC curve depending on temperature. The working principle of TSC technique is shown as follows: first of all, apply an unchanged electric field to polarize