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Impacts of cold atmospheric plasma on oleic acid

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Abstract

Impacts of atmospheric plasma on chemical bonding in oleic acid are investigated. Oleic acid was exposed to a plasma generated either from a DBD device and a plasma jet devides. For the DBD plasma treatment, 0.5 ml oleic acid was dropped on a plate and treated by direct atmospheric exposion plasma for 10 minutes, 20 minutes, 40 minutes, 60 minutes or 180 minutes. For the plasma jet, an air-base plasma jets was generated and directly flow into 50ml oleic acid for 60 minutes, 120 minutes and 180 minutes. Oleic acid droplets tended rapprochement after treatment, implying that oleic acids hygroscopicity increases. Attenuated total reflection - Fourier transform infrared spectroscopy (ATR- FTIR) was employed to analyze the absorption of different bonding after treatment. The noteworthy results show that the reduce of double bond C=O in carboxylic acid group at peak 1780-1700 cm $^{-1}$ was found. In addition, an increase of C=C bonding at peak 1640- 1620 cm^{-1} was found. Moreover, the absorption of C-O, CH, CH$_2$, CH$_3$ also change. It suggested that the atmostpheric plasma can effect double bond in oleic acid, resulting in the formation of esters, ethers and probably polymerization.

Keywords*:* DBD plasma, Plasma jet, oleic acid, ozonolysis.

1. Introduction

Plasma technology is one of the key future technologies with a potential of innovative long-term solutions in many areas. It provides an interesting solution which responses to high demands on quality, productivity, environmental compatibility, precision and flexibility. It has important contribution to the growth areas of electronics, agriculture, machine and tool-making industries, energy technology, the optics industry, and textile, environmental, and medical technology. Ingeneral, plasma usually applied to the removal of pollutant or pathogenic factor. Using plasma as a catalyst, it can accelerate the reaction in chemical industry is interesting and could be useful[1,5].

In this study, the basic material in organic chemical- oleic acid (C18H34O2) was directly exposed to DBD(dielectric barrier discharge) plasma and plasma jets in atmospheric pressure to observe the effect of cold plasma on oleic acid. Oleic acid has benefical effect to human heath, disease[2]. It usually using in organic chemical because it contains the structure of typical fatty acid, alkenes. Study of oleic acid usually uses for further research about cooking oil, typically olive oil, which contains 70% oleic acid [7].

Ozonolysis oleic acid was researched in Hung et.al by reaction of oleic acid and ozone[2]. Results of this reaction are potential products as nonaal acid, azelaic acid and the polymerization, which can apply in cosmetic. However, this reaction takes a long time (3 days) and small scale, which suggests to use plasma as improve environment for reaction [2].

Plasma is an oxidized gas, which has conductive assemblies of charged particles, neutrals and fields that exhibit collective effects. It contains electrical currents, motivated and free electrons, free radicals, mainly are reactive oxygen species (ROS) and reactive nitrogen species (RNS) [3]. The reaction oleic acid with ozone was studied in recent years. The reaction proceeds via the addition of ozone to the double bond of oleic, which yields a primary ozonide. The high energy ozonide rapidly decomposes. The associated products would be 1-nonanal, nonanoic acid, azelaic acid, oxo-nonanoic acid and an unidentified group contain ester group and polymer group [2].

Moreover, DBD plasma is cold plasma which was oftenly used in a surface treatment. It can modify the surface of rice seeds, resulting in accelerated germination and enhanced water imbibition[1]. This result suggests to using plasma to modify oleic droplets surface properties lead to greater hygroscopicity. In addition, It can increase tendency of atmospheric particles to take up water and nucleate clouds if it applies in atmospheric environmental [2].

In order to have more perspective on the impact of cold plasma to oleic acid, the impacts of plasma jets to oleic acid also study. Plasma jets was known as a higher concentration of plasma and can apply in large-scale experiments. The results of chemical change in oleic acid after treatment by plasma provide more information about the impacts of plasma on oleic acid.

This study addresses the foregoing on question. Attenuated total reflection infrared spectroscopy (ATR-IR) method, which base on the absoption of sample to evanescent wave to know chemical bonding of sample was employed. This result gives the change in chemical properties of oleic acid. The location of droplets before and after treated give the change of hygroscopicity of oleic acid.

2. Experimental approach.

2.1. DBD plasma system

Oleic acid droplets (>99% purity) are prepared with a micropipette and dispensed onto a single-crystal glass surface. The droplets diameter is controllable from 1 mm to 3 mm. In each experiment, 0.5 ml of oleic acid is divided into 20 droplets. Each sample was treated in DBD plasma system in 10 mins, 20 mins, 40 mins, 60 mins and 180 mins.

DBD plasma system includes 1 electrical source connect with 2 electrodes, which has at least one electrodes was cover by isolated material, in this case, we used glass. Oleic acid, which was dropped onto a petri dish shape of diameter 10 cm was set up between 2 electrodes. When applied high voltage, plasma was generated between 2 electrodes and was effected to oleic acid.

The electrical source is a laboratory-made free running oscillator which was set at frequency 5.5 kHz and voltage at 2 kV. Two electrodes contain one copper electrode and one steel electrode. The experimental schematic was showed in figure 1. The experiment was done in atmospheric pressure and room temperature.

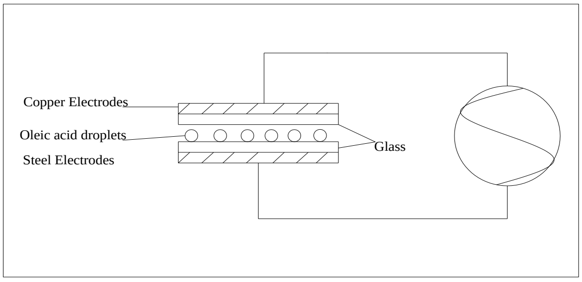


Fig. 1 DBD plasma schematic

In order to see the change of density and hygroscopic of droplets, a picture of oleic acid droplets was taken before and after exposure.By dropped oleic acid onto FT-IR crystal and analyze by attenuated total reflection infrared spectroscopy (ATR-IR) was used to looking the change of chemical structure of oleic acid before and after treatment.

2.2. Plasma jets

Plasma jets was set up at the atmospheric pressure and the room temperature. The system includes 1 inner electrodes, 1 external electrodes cover one glass tube, which has diameter 2 mm, connect with 1 electrical source. The glass tube also connects with a mini air pump, which supplies 5 liters/ minutes flow through discharge area and dumps into a flask, which contains 50ml purity oleic acid. When the gas flow through the discharge past between 2 electrodes, gas was excited and converted to plasma. The schematic of experiment was shown in figure 2.

After treatment, oleic acid was analyzed by ATR-FTIR technique. The results were compared with results before treatment and results of oleic acid treated to DBD plasma.

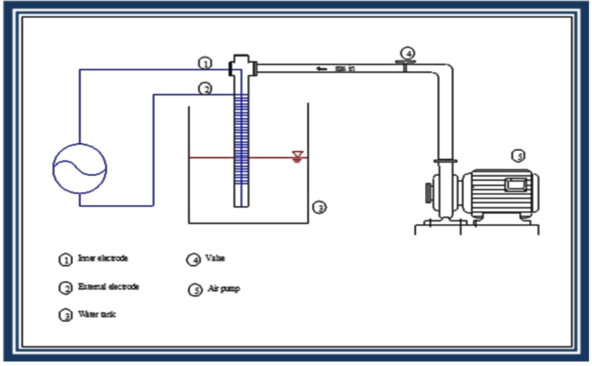


Fig. 2 Plasma jets schematic

3. Results and discussion

3.1. DBD plasma

Changes in viscosity and density of oleic acid droplets is found after exposing to DBD plasma, which responds to the change in hygroscopicity. Fig. 3 show the oleic droplets before and after treatment. It can be seem that oleic acid droplets tend rapprochement. Most noticeable with sample treated in 3 hours.

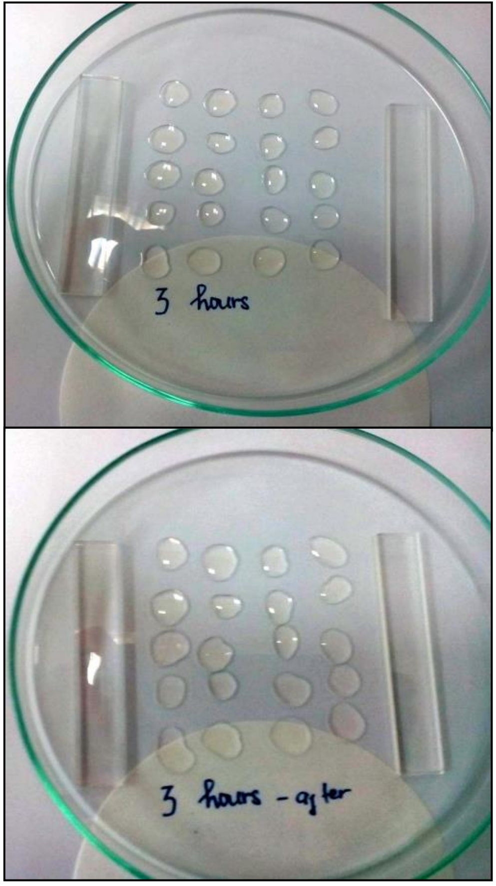


Fig. 3 Locations of oleic droplets before (above) and after 3 hours (below) treatment by DBD plasma.

These photos indicate the increasing density oleic acid droplets during plasma processing. Thus it affects the estimation of bulk hygroscopicity parameter in atmospheric environmental. Besides, the change in droplets density also plays a vital role in the mass concentration conversion and mass closure calculation[4].

In this experiment, the increased density of oleic droplets are believed to be affected by the bombardment of electrons in the plasma production process breaks the surface structure of oleic acid droplets increases hygroscopic and be influenced by oleic acid ozonolysis process creates massive molecules. Besides, active in oleic acid ozonolysis also caused an increase in intermolecular bonding associated with the formation of carboxylic acid, ketone, aldehydes and other oxygen- bearing chemical functionalities. However, this effect is not really clear, especially when treatment time less than 3 hours. These impacts need to be confirmed because the density of oleic droplets may increases by the increase of temperature during experiment [9].

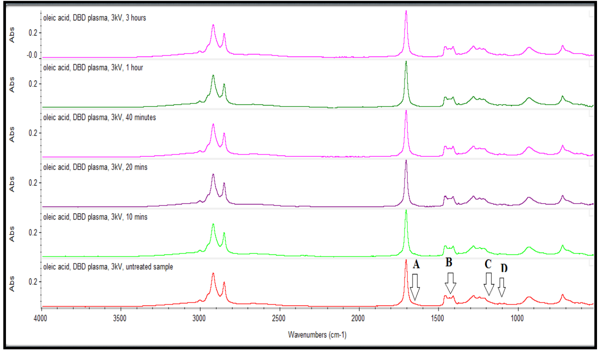
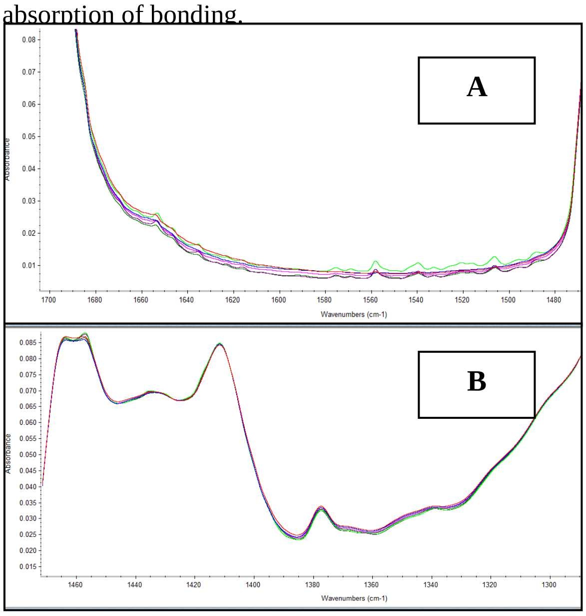


Fig. 4 Infrared spectra of oleic acid before and after treated to DBD plasma

The infrared spectra recorded with different treating time show in figure 4. The IR spectra show that no new peak present after treatment but the amount of bonding in samples before and after treatment were different. It suggested that there are some reaction were occuring during experiment, such as breaking the bonding or change spatial structures of oleic acid molecules. Although the product chemical structure did not identify, the IR spectra show the change in chemical structure based on the light absorption of bonding.



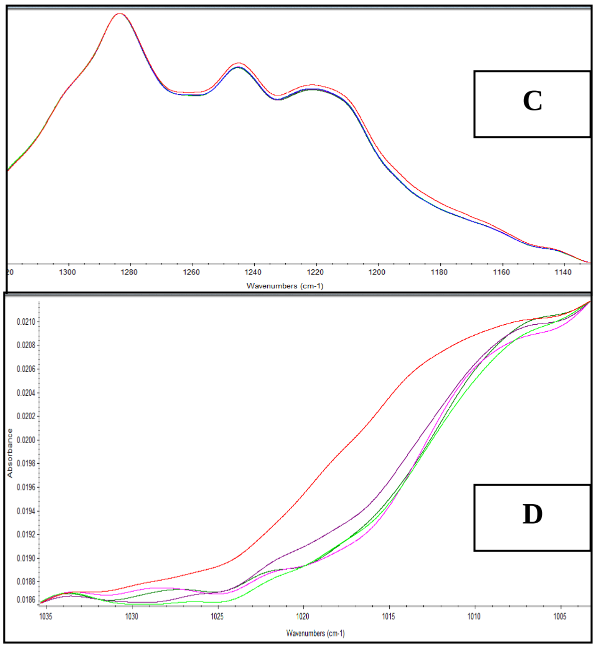


Fig. 5 Detail of oleic acid infrared spectra before and after treatment at the peak showed in fig. 4.
(Red line is infrared spectra of untreated oleic acid).

As expected, the absorption at region 1780 cm-1 to 1710 cm-1, which responding to C=O bonding in carboxylic was reduced. The increasing of absorption at peak 1680 cm-1 - 1620 cm-1 represent to C=C bonding also recorded. The absorption decreased at peak 1460 cm-1, which respond to CH2 bending mode, and increased at peak 1375cm-1 , which indicated for CH3 bending can suggest for the breakdown molecules while treating to plasma. Peak 1210cm-1 – 1140 cm-1 and peak 1030 cm-1 - 1000 cm-1 has broad reduced, this peak showed the results of C—O-C bonding in ester or ethers. All of these results support the theory that DBD plasma breaks oleic acid molecule and react to double bond C=O and C=C of oleic acid, results is primary ozonide in ozonolysis process.

The most appropriate assumption is the reaction of oleic acid, ozone and nitrate radical. Ozonolysis process between oleic acid, ozone and nitrate radicals was reported by Hung *et al*, which the reaction occurs through many steps. The first phase is broken double bond, resulting in primary ozonide [2].

3.2. Plasma jets

In previous experiments, the double bond in oleic acid was changed after exposure to DBD plasma. However, there are too many factors can effect that results, such as the increase of temperature during generated plasma. In order to confirm the effect of free radicals in plasma to oleic acid, the plasma experiment was set up with large scale. Plasma jets has lower gas temperature than DBD plasma, so the effect of temperature, in this case, can ignore [7].

Furthermore, DBD plasma system had several mm scale, which caused some trouble for future research as not enough sample, the burning or evaporation of sample, etc… Doing experiment in large scale with plasma jets system help us fix these problems and have more viewpoint about the impact of cold plasma to oleic acid.

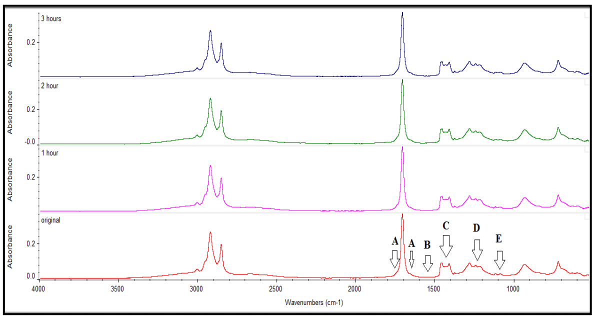
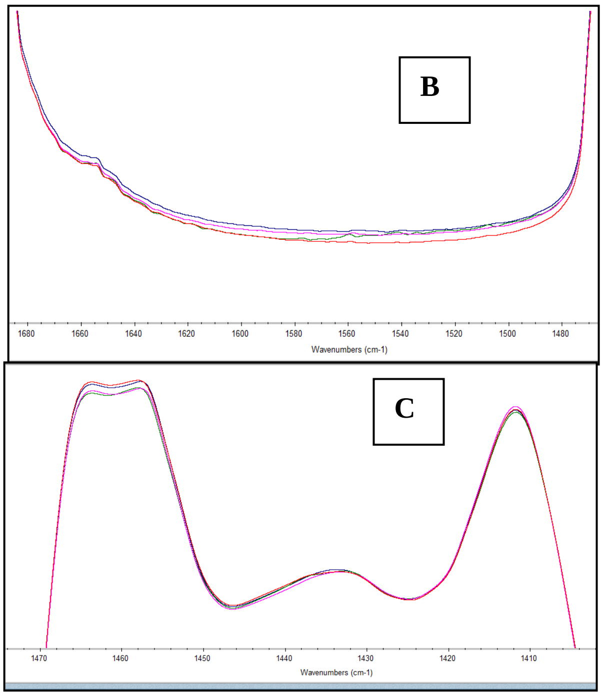


Fig. 6 Infrared spectra of oleic acid before and after treated to plasma jet.

The infrared spectra of oleic acid before and after treated to plasma jet was shown in figure 5. In the similar trend with DBD plasma system, there is no new peak was recorded but the absorption of bonding was changed. The reduced of absorption in peak 1780 cm-1 -1720 cm^{-1} and peak 1700 cm^{-1} - 1650 cm^{-1} (peak A, results not show) represent to the decreased of C=O bonding was recorded. Absorption of peak 1640 cm-1- 1620 cm^{-1} also increased but more broadly, in comparison to DBD system.

The results also recorded the decreased at 1460 cm^{-1} – 1400 cm^{-1} (CH2 bending), the increased at peak 1370cm^{-1} - 1320 cm^{-1} (CH3 bending), the reduced near 1250 cm^{-1} (C-O stretch), reduced at 880 cm^{-1} (C-H meta- bend) and the increase at 940 cm^{-1} (C-O-C) similar to sample treated with DBD plasma. However, oleic acid treated to plasma jets has increased absorption at peak 1120- 1080 cm^{-1}, which also respond to C-O bonding in ether.



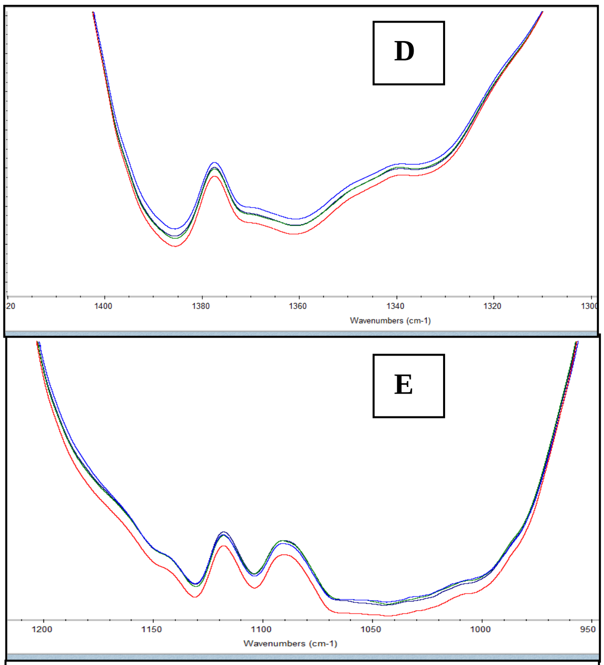


Fig. 7. Detail of oleic acid infrared spectra before and after treat with plasma jets at peak showed in fig. 6(Red line is untreated oleic acid spectra).

The results suggested that ester and ether were formed during the experiment and lead to the change in CH2, CH3 absorption. Moreover, oleic acid also can breakdown in experiment, which explains the change of absorption in C=O, C-O, CH, CH3, CH2 bonding

. 4. Conclusion

In this study, the effect of atmospheric plasma on oleic acid was observed by both surface modify and chemical structure. After treated with DBD plasma, oleic acid droplets had more densely density and large surface area. It means after treatment, oleic droplets become closer. It suggests that DBD plasma can apply in atmospheric environmental to decomposition organic compound in heterogeneous reaction. However, this effect is small and need to confirm the mechanism. Both DBD plasma and plasma jets change the chemical structure of oleic acid. Results are the change in double bond C=C and C=O, the increased of C-O-C bonding. It suggested that oleic acid molecules were reacted with ozone, oxygen species radical, results is ester and ethers, polymer was formed. The change of absorption in CH2, CH3, CH bonding also indicated the breakdown of oleic molecules.

5. Acknowledgments

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