

# Development of non-thermal atmospheric pressure plasma system for surface modification of polymeric materials

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**Abstract.** Non-thermal plasma has become one of the new technologies which are highly developed now days. This happens because the cold plasma using the principle of generated reactive gases that have the ability to modify the surface properties of a material or product without changing the original characteristics of the material. The purpose of this study is to develop a cold plasma system that operates at atmospheric pressure and investigates the effect of cold plasma treatment to change the surface characteristics of the polymer material polyethylene (PE) at various time conditions. We are successfully developing a non-thermal plasma system that can operate at atmospheric pressure and can be run with Helium or Argon gas. The characteristics of plasma will be discussed from the view of its electrical property, plasma discharge regime and operation temperature. Experiment results on plasma treatment on PE material shows the changes of surface properties of originally hydrophobic material PE becomes hydrophilic by only few seconds of plasma treatment and level of hydrophilicity become greater with increasing duration of plasma treatment. Confirmation of this is shown by the measurement of contact angle of droplets of water on the surface of PE are getting smaller.

## 1. Introduction

Plasma can be referred to as the fourth phase element after solid, liquid and gas phase. Unlike the normal gas phase which electrically neutral, plasma contains components of the atomic nuclei (ions) and electrons as the charged particles which have been separated because of the external energy received and have a reactive nature. Plasma can be formed naturally as happens in the sun or the elements of the stars in the sky. Plasma can also be formed by providing a high energy from proper electricity into a gas medium that makes the gas is undergoing a dissociation and ionization processes. Depending on the amount of energy transferred the transformation of the neutral gas into negatively and positively charged particles can be occurred as a part or a whole processes. The fully transformation will lead to the generation of high temperature or thermal plasma in which the temperature of all plasma components (ions, electrons, reactive species and neutrals) are the same. If the transformation occurred partially, it can allow the formation of low temperature or non-thermal plasma in which the temperature of electrons is several orders of magnitude higher than the temperature of ions or neutral species. When the thermal plasma technology has its application history for more than three decades, currently there is a much interest in the development of non-thermal plasma with their applications, specially the plasma discharge that can be generated at atmospheric pressure instead of conventional non thermal plasma at vacuum condition.



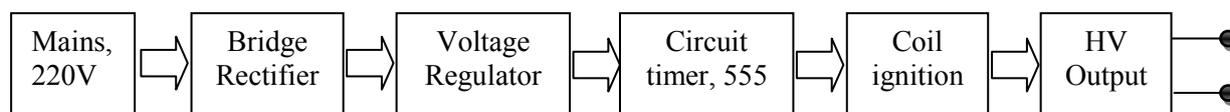
Much works have been done on the development of non-thermal plasma at atmospheric pressure plasma. Advantages both from economic and operational compared to the low pressure one have led to the variety development of non-thermal atmospheric pressure plasma as a recent trend of focus research [1]. Atmospheric pressure plasma is also generates the reactive species to modify the surface characteristics of material with the comparable result as it treats with low pressure plasma [2]. However, most of those studies were using radio frequency (RF) power supply [3-5] and microwave power supply [6, 7]. The present work deals the development of non-thermal plasma at atmospheric pressure by using a high voltage power supply (HVPS) and also discussing the application of the plasma system to modify the surface of PE film material. Development of this type of HVPS brings the advantage at which the ionization process occurred partially in the gas flow, so that the generated plasma discharge has relatively low temperature during operational. This type of plasma is suitable to be used to change the characteristic surface of particularly the thermal-sensitive material such as polymers or textile materials without any thermal damage to the irradiated surface.

Modification of the surface characteristics of the material by plasma techniques include the presence of strong interaction between the reactive species, electrons and ions formed in the plasma with the upper surface of the material. There are two things that will occur due to interaction of the material with the plasma, namely: plasma activation process, which usually involves a discharge of plasma without working gas that can form a polymer layer, such as argon gas, oxygen, nitrogen and others. The second one is the plasma polymerization process, in which the method of plasma treatment is using a working gas that can lead to polymerization process, such as gas sulfur hexafluoride ( $\text{SF}_6$ ) gas tetrafluoromethane ( $\text{CF}_4$ ) and others. Result of plasma polymerization is usually in the form of thin film solid formation the surface of the material. Both of two typical plasma processes mentioned above are a process that involves plasma with specific objectives to change the surface properties without changing its bulk characteristics, including the mechanical properties of the material. In this paper the development of home-made cold plasma generator and its system design at atmospheric pressure will be presented. Some characteristics of the generated plasma will be investigated and the plasma utilization in modifying the surface of polymer materials will also be discussed.

## 2. Experimental

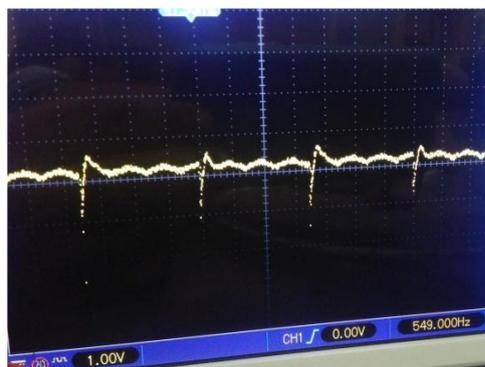
### 2.1. Plasma generator

Atmospheric pressure plasma generator in this works was typical high voltage power supply, developed using 555 timer circuit coupled with ignition coil. Figure 1 shows the simplified block diagram of high voltage generator for generating the non-thermal plasma.



**Figure 1.** Block diagram of high voltage generator for atmospheric pressure plasma system.

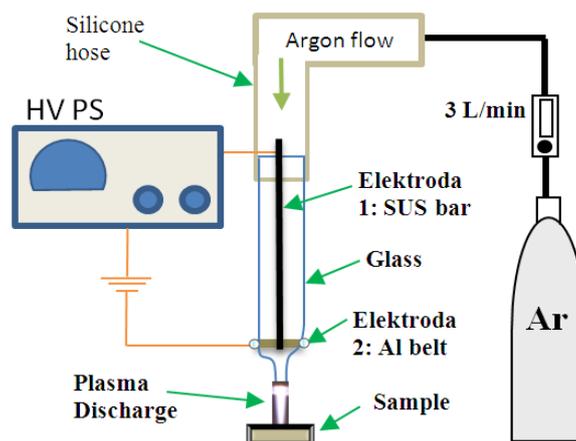
The voltage waveform of plasma generator was measured by using Hantek DSO5072P digital oscilloscope and a high probe PD-28 with the attenuation ratio of 1000:1. Figure 2 displays the voltage waveform during plasma discharge by using Argon gas at the flow rate of 3 l/m. It displays the discharge voltage about 3 kV with a rise time 1.82 ms.



**Figure 2.** Voltage waveform during plasma discharge using 3 l/m Argon gas.

### 2.2. Plasma treatment for surface modification

Figure 3 shows a schematic diagram of experimental setup used for surface modification of polymeric material. High Voltage Power Supply (HVPS) connected to the SUS bar electrode which is surrounded by a glass tube. The other electrode of aluminum belt was placed at a distance of 7 mm from the edge of glass tube and connected to the ground. The stream of Argon gas from the opposite side was used for plasma generation and flowed through the glass tube at a rate of 3 liters per minute. For the purpose of exploring the application of this non thermal plasma system in modifying the surface of the polymer material, a 3 mm in thickness of polyethylene (PE) sheet was placed on the sample holder with a distance from plasma discharge nozzle as far as 2 mm. In order to verify the change of surface properties of PE sample, analysis of the water contact angle will be used in this study. A drop of water will be deposited on the surface of the material samples before and within a minute after plasma treatment. Contact angle will be measured from the water droplets by taking the image by using a digital microscope at a specific angle. Plasma treatment was conducted at applied voltage 3 kV by using argon gas at various period of time to know the effect of treatment time on PE wettability, which can be confirmed by measuring the decreasing of contact angle.



**Figure 3.** Schematic diagram of non thermal plasma system at atmospheric pressure for surface modification of polymeric material.

### 3. Result and discussion

A plasma system that operates at atmospheric pressure was successfully developed with the electrical energy source in the form of high voltage power supply is based on a vehicle ignition coil. Pictures of the plasma generated by the system in this study can be seen in figure 4 with the difference of working

gas. The length of the plasma can reach as long as 6 mm with the usage of 3 l/m of working gas. The discharge appears in the uniform phase (glow discharge) in helium based and seems to be in the form of filamentary when using argon gas. Due to more beneficial in cost and having better energy transfer efficiency than helium [8], argon gas will be used for the utilization of the plasma system in this study.

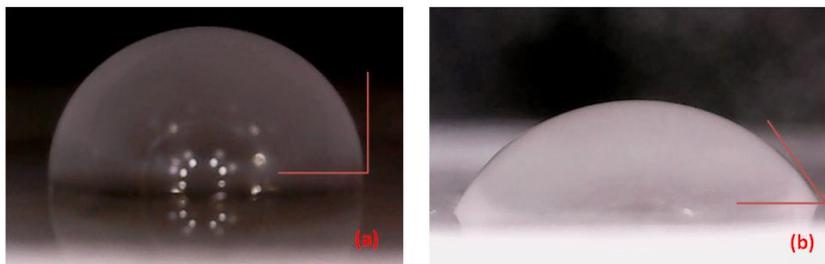
The operational temperature of the atmospheric pressure plasma can reach 35°C as measured after 120 seconds time of discharge and no significance increase observed afterward. This indicates that the characteristic of the resulting plasma is the type of non-thermal atmospheric pressure plasma. The plasma with this typical characteristic is very important for the treatment of materials with the purpose to modify the surface properties, especially for the surface treatment of the heat-sensitive material such as a polymeric material.

Application of the developed plasma discharge system above is proposed to modify the surface characteristic of polyethylene (PE). This material is preferred because PE as one of the most utilized in applications has excellent properties such as: low cost, low density, high flexibility and resistance to chemical liquids. However, the utilization of PE sometimes meets its limitation because PE also has a low surface energy properties that making PE has low adhesion properties and hydrophobic. Treatment with plasma technique is intended to improve wettability and adhesion properties of the PE surface as a potential replacement for traditional treatment that using chemical solution in a very unfriendly environment. Surface modified PE is generally known to bring the advantages into the wide area of practical application, such as: increasing its performance as a material for printing/painting in the packaging industries, enhancing the adhesion/bond ability of glue or coatings and improving the biocompatibility in the artificial components in biomedical applications [9, 10]. The surface modification of the polyethylene in this study was conducted from 10 to 60 seconds with atmospheric pressure plasma treatment. After that, a droplet of water from a pipette was dropped on the surface of the material, and the water contact angle was measured. The contact angle of plasma treated PE would be then compared with the non-treated or original one.



**Figure 4.** (a) Picture of plasma in Helium and (b) plasma discharge with Argon gas.

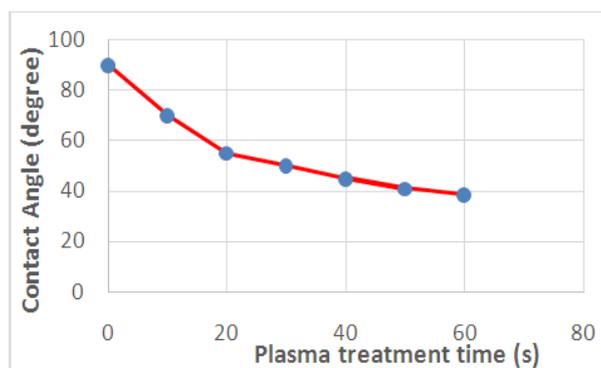
Figure 5 shows a picture of a drop of water beads on the surface of PE before (a) and after (b) treatment of argon plasma at atmospheric pressure. Visible differences in the contact angle as seen in that figure indicated by the decreasing of contact angle of water bead from 90° to 55° after plasma treatment for 20 seconds. This is also as a confirmation of the increase of wettability properties of the modified surface of PE.



**Figure 5.** Contact angle of water bead on the surface of PE (a) original, and (b) after 20 seconds of plasma treatment. (Argon gas flow: 3 l/m, applied voltage 3 kV, treatment time: 20 s)

Figure 6 shows a graph of the decreasing in contact angle after various argon plasma treatment times at atmospheric pressure. From that figure, it can be seen that the plasma treatment for 60 seconds can make changes in the characteristics of the hydrophobic surface becomes hydrophilic PE (like water) to decrease the contact angle of  $90^\circ$  in the PE becomes  $38.5^\circ$ . From the graph above also shows that the first 20 seconds of plasma treatment took quite significant effect on a decreasing in contact angle, followed by a relatively stable decrease in the contact angle by addition of plasma treatment time.

The transformation in surface properties of the naturally hydrophobic PE into hydrophilic through contact angle measurements can be explained as follows: plasma discharge containing positive ions, electrons, free radicals and other reactive elements will bombard the surface of PE with each energy possessed by the plasma elements. The reaction that occurs between the plasma and the material causes the PE surface become activated. When the plasma discharge is drop off, the interaction between activated PE surface with the ambient air or atmosphere led to the creation of new polar functional groups such as: C=O, OH, COOH and other oxygen containing function groups on the surface. Those new polar groups provide stronger bond with water droplets (increasing of the wettability). The more time needed to expose the PE surface with the plasma discharge, the more oxygen functional groups will be generated. In consequence, the PE surface become more polar and make the water contact angle turns into the decreasing, indicated by the level of the water droplets on the surface of the material become wider. This is how the transformation process of PE surface has been occurred from hydrophobic into the hydrophilic. This finding is in accordance with the results of Kun et al [11] when treating the PE surface with coplanar barrier discharge. In that case, dramatic decrease of water contact angle was happened during the first 20 seconds and found the new groups of COO-, C=O and -OH through measurement by means of FTIR.



**Figure 6.** The graph of decreasing in contact angle by increasing plasma treatment time.

#### 4. Conclusion

An atmospheric pressure plasma system has been developed using ignition coil-based high voltage power supply. This system can sustain the plasma discharge either by using helium and argon as working gas. It was found that the temperature of the discharge can achieve around 35°C even in the long run operation and this type of non-thermal plasma may suit for application in modifying the surface of thermal-sensitive material like PE polymer without altering its bulk properties. In attempt on exploring the utilization of the plasma system for modifying PE surface, the results showed that the PE surface can be altered into hydrophilic phase by treating it with the plasma for 60 seconds. This has been confirmed by the decreasing its contact angle from 90° to 38.5°. The present results may provide the promising application in modifying surface of thermal-sensitive material in a very short time of treatment.

#### References

- [1] Nehra V, Kumar A and Dwivedi H K 2008 *Int. J. Eng.* **2** 53-68
- [2] Noeske M, Degenhardt J, Strudhoff S and Lommattzsch U 2004 *Int. J. Adhes. Adhes.* **24** 171-7
- [3] Chun H, Wei C M, Tsai C Y, Hou W T, and Juang R S 2013 *Surf. Coat. Technol.* **231** 42-6
- [4] Li Y P, Zhang Z C, Shi W and Lei M K 2014 *Surf. Coat. Technol. A* **259** 77-82
- [5] Igor N, Anton P, Zdeno S, Matej M, Maria O, Marian V, Jan S, Ivica J, Angela K and Miroslav S 2015 *Vacuum* **119** 88-94
- [6] Mengyao Y, Baoming Z, Kunyan J, Xiaoming Q, Zhiwei X, Kunyue T, Lihuan Z, Jiajun W and Yanan J 2015 *Appl. Surf. Sci.* **327** 93-9
- [7] da Maia J V, Pereira F P, Dutra J C N, Mello S A C, Becerra E A O, Massi M and Sobrinho A S S 2013 *Appl. Surf. Sci. B* **285** 918-26
- [8] Kasih T P, Kuroda S and Kubota H 2007 *Plasma Processes Polym.* **4** 648-53
- [9] Kazimi M RAhmed I and Faizal C K M 2011 *Proc. Int. Conf. on Chemical Innovation (Terengganu)* (Malaysia: Terengganu/ TATI University College) pp 203-6
- [10] Pandiyaraj K N, Deshmukh R R, Ruzybayev I, Shah S I, Pi-Guey S, Halleluyah Jr M and Halim A S 2014 *Appl. Surf. Sci.* **307** 109-19
- [11] Kun W, Jian L and Shi-qing W 2012 *Proc. 2<sup>nd</sup> Int. Conf. on Electronic & Mechanical Engineering and Information Technology (Liaoning)* (France: Paris/Atlantis Press) pp 1038-42