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Examples of Organic Substances Treatment by Gliding Arc Plasma

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Abstract

The aim of this contribution is the demonstration of several applications of atmospheric pressure discharge for treatment of biological and biomedical substances. Surface tension enhancement of medical devices for better labeling can be assigned to traditional applications. Treatment of rabbit fur as the first step of felting in a process of hat production is described. The goal of this experiment was replacement of dangerous wet chemical process by ecological friendly dry treatment. The investigation of possible utilizing for organic dye decomposition in water solution in synergy with photocatalytic layer P25 Degussa was also performed. A pilot experiment of barley seeds treatment for germination stimulation is given as a third example. Plasma treatment of seeds proved to influence the germination of various types of seeds.

Introduction

Many types of cold plasma source are widely used for feasible industry applications. New type of atmospheric pressure plasma source has been developed from the last decade of the 20th century. It is cold non-equilibrium plasma source based on the principles of gliding arc. The principle of gliding arc was described in detail in [1]. The either DC or AC arc ignites in place of the minimal gap between two high voltage electrodes made of various materials (stainless steel, copper, aluminum, etc.). The arc discharge is forced by relatively strong carrier working gas flow to glide along diverging electrodes and it causes increasing of the arc length. Exceeding critical length the transition into non-equilibrium regime occurs. After the decay of the non-equilibrium discharge, the arc evolution repeats from the initial break-down.

The atmospheric pressure gliding arc has been already used in lots of industrial applications such as organic dye decomposition [2-4], air depollution, UV generation [5], activation of organic fibers [6], volatile organic compounds decomposition [7], reactive species formation [8], and others. One of the traditional applications of cold plasma is surface tension enhancement of medical devices for better labeling. Such devices are mostly made of plastic materials that are more or less polyethylene (PE), polypropylene (PP), or polyurethane (PU) modifications, for instance Pellethane®2363–65D TPU used for medical catheters production [9]. There are some other applications in this field focused mainly on the biological materials treatment that have not been carried out yet, for instance pre-treatment of rabbit fur for replacing of dangerous wet chemical method as first step of felting process.

Experiment

The schematic drawing of the plasma jet device experimental setup is in Figure 1. The discharge is generated by high voltage transformer (10 kV/160 mA) between two diverging copper electrodes of minimal gap 5 mm. The electrodes have semicircle shape. The power source is operated at frequency 50 Hz. The jet cover exceeds 5 mm over the tips of electrodes. Compressed air is commonly used as carrier working gas and it goes through the gas inlet of 1 mm diameter into the space between electrodes. The overpressure of the air was maintained at approximately 6 bars in every experiment. The air flow can be changed in the range from 20 SCFH (standard cubic feet per hour) to 80 SCFH by an air flowmeter.

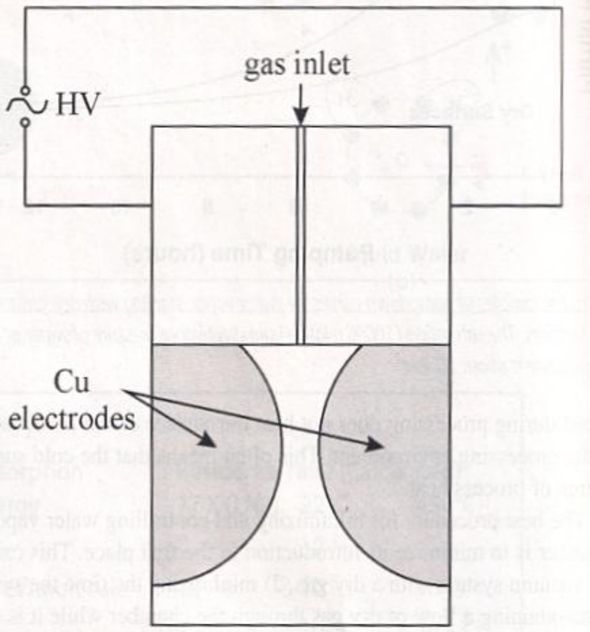

Figure 1. The schematic drawing of the plasma jet device experimental setup.

The standard experiment for testing of the device was carried out. The equipment was used for surface energy enhancement of PE surface to determine optimum parameters of the device for the highest process efficiency achievement. PE surface samples cleaned by ethanol in advance were exposed by the discharge for different treatment time (30, 90 or 180 second) and air flow (from 30 SCFH to 60 SCFH). In some experiments water vapor addition was applied. After samples treatment water contact angle measurement was applied by commercial device SeeSystem. It is based on the investigation of small water droplet shape on the tested surface. The droplet volume was 10 ml and its temperature was 22°C. The water contact angle is computed by software supplied by SeeSystem producer. At least three small droplets situated in different places on tested surface were applied for each sample and the measurement of the droplet dimensions by software was five times repeated for each droplet. Then average value of every measured angle for one sample was established as final water contact angle.

The treatment of rabbit fur for following felting in the process of hat production was performed. Cut hairs were used for hand test of felting. The test consists in shaking 0.5g of cut hairs in sulfuric acid water solution of pH equal to 2. The total time of shaking was 20 min. The visual qualitative analysis and measurement of felt object diameter by caliper were carried out.

The organic dye decomposition was investigated. Acid Orange 7 (AO7) was used as a model organic dye. The initial concentration of AO7 was 20 mmol/l in each performed experiment. The AO7 concentration decreasing after treatment was determined by UV/VIS spectrometry from absorbance at 487 nm. Finally natural logarithm of the initial and final concentration ratio was taken as a main indicator of the system degradation effect.

Seeds of barley (Hordeum vulgare L.) were chosen as a model type of seed for treatment. The seeds were pre-treated by gliding arc device slightly different from the device described above. The description of the apparatus is in [10]. Three different times of plasma exposition were used, in particular 180s, 300s, and 600s.

The germination and early growth tests were performed on Petri dishes under the same laboratory conditions for six days. Five replicates and 150 seeds per one of plasma treatments were tested. The number of germinated seeds, the length and weight of sprouts were monitored. The test design was same as in [10] (more details there).

Logarithmic transformation (y=log(x)) of the obtained data was used for normalization. The influence of the plasma pre-treatment on barley seeds was evaluated through the t-test. All the statistical tests were done at the significance level of 0,05 and analyzed by the program STATISTICA.

Results And Discussion

Results summary of the optimum parameters investigation to achieve the best influence on water contact angle on PE surface are shown in Figures 2 and 3, respectively, Figure 2 shows the dependence of water contact angle on PE surface on carrier air flow for different water vapor addition systems. It is evident that presence of water vapor in different areas of plasma strongly influences amount of active particles that cause surface tension changes of PE surface. Vapor addition into the flowing plasma under device cover appeared much better than direct addition of water vapor into the gas flow before it goes through the gas inlet. In addition passing vapor added in carrier gas flow through area between electrodes caused some problems with discharge ignition and consequently led to very small surface tension changes even lower than in case of experiments without water vapor.

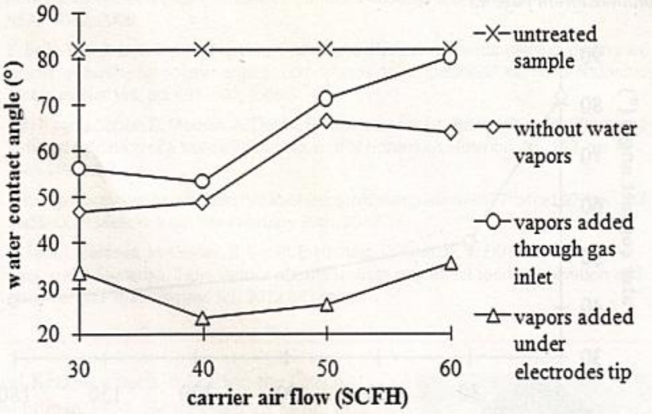

Figure 2. Dependence of water contact angle on carrier air flow for PE surface for different water vapor addition systems (treatment time 30s, distance of PE from cover edge 15 mm).

The water contact angle on PE surface depending on the treatment time is depicted in Figure 3. It is obvious that surface tension is strongly changed immediately during short time from the treatment beginning. On the other hand ongoing treatment did not cause so high surface tension changes in comparison with the changes during the first half of minute. In addition it can cause unwanted thermal changes of the treated material due to its heating up, especially for plastic material with lower thermal endurance.

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Examples of Organic Substances Treatment by Gliding Arc Plasma

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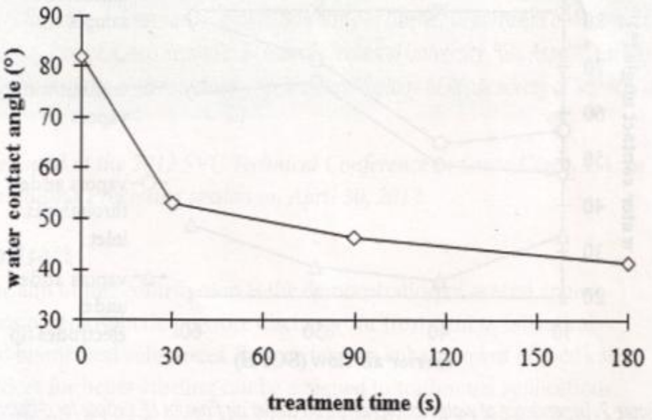

Figure 3. Dependence of water contact angle on treatment time for PE surface (air flow 40 SCFH, distance of PE from device cover 15 mm, water vapors added through gas inlet).

Very interesting results can be seen in following Figure 4. It performs the comparison of several felt objects made from hairs of the rabbit fur. The object (a) was felt from natural rabbit fur without any pretreatment (chemical or by plasma). It is evidently low-tenacious and very "hairy". The diameter measurement of this object was very problematic and it was only estimated to 28 mm. Object (b) was felt from the rabbit skin prepared by standard chemical wet process by the hat producer. It is obvious that this object is much more compact than the first one. Its diameter was 19,3 mm. The third object (c) was felt from plasma treated fur. Its diameter is 24,0 mm and its consistence is comparable to the object (b).

The synergy effect of active species produced by the discharge, emitted UV light and photocatalytic layer immersed into the organic dye water solution were studied. For comparison, the Petri dish with the solution was covered by laboratory glass transparent for lights of wavelength 300 nm or higher in one experiment to prevent passing high-energetic UV light into the solution. In addition in such case the glass inhibits direct interaction of species formed in active plasma flow (ozone, electrons, ions etc.) with the solution. In some experiments the photocatalytic layer P25 Degussa immersed into the solution was used.

Figure 5 shows synergetic effect of various phenomena. Natural logarithm of the initial and final AO7 concentration ratio is depicted. Each of columns corresponds to different experimental conditions. The column (a) performs solution irradiated only with the low-energetic UV light from plasma and ambient background. It is evident that only low-energetic UV light on its own cannot decompose organic dye and it has to act in synergy with the other agents. The column (b) shows similar conditions as the first one but in addition the photocatalytic layer immersed into the solution was used. The layer is activated by low-energetic UV light but the activity of the layer and also decomposition ratio are relatively low. When covering glass was taken away the decomposition increased rapidly, as can be seen in columns (c) and (d). Experimental conditions of (c) correspond to those from (a), and conditions of (d) are very similar to (b). It is very evident that synergy effect of simultaneous incidence of ozone, active species and wide range of UV light (mainly high-energetic) can enhance the decomposition process. The photocatalytic layer activation by high-energetic UV light was of a higher influence to dye decomposition in comparison with the low-energetic one as can be seen from (d).

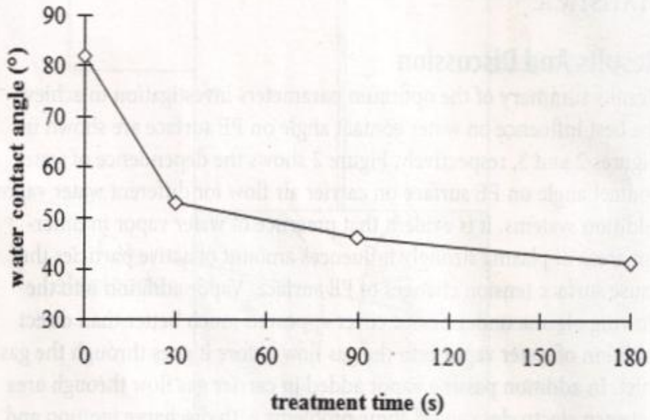

Figure 5. Organic dye decomposition ratio comparison for different experimental condition. (a) only low-energetic UV light, (b) low-energetic UV light in synergy with photocatalytic layer, (c) wide-range UV in synergy with ozone and active species, (d) synergy of wide-range UV, ozone, active species and photocatalytic layer.

The typical results of barley seeds germination are summarized in Table 1. Pre-treated growing barley seeds had longer roots and shoots and highest weight of root than a control sample. The negative impact was found only in weight of shoot after exposure of 3 min and 5 min. The best germination was shown at seeds modified for 5 minutes (105 %, t-test, P<0,25). No significant differences were found between the weight of shoot and the control.

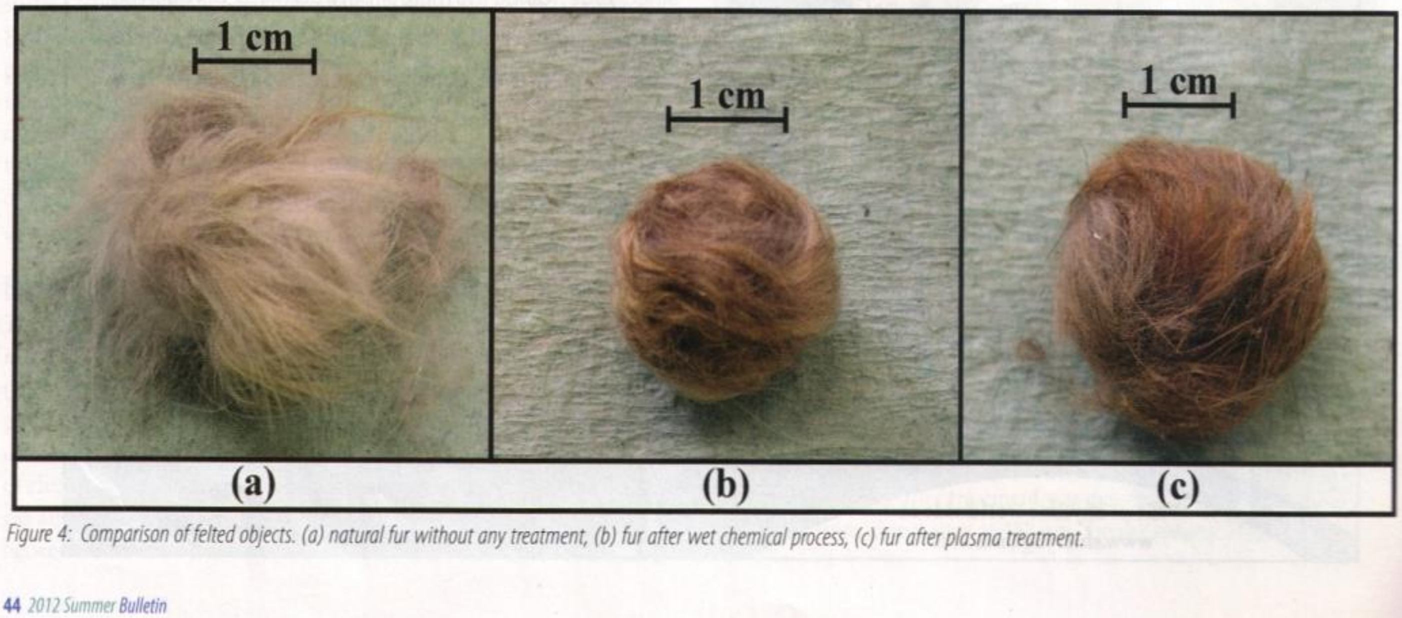

Figure 4: Comparison of felted objects. (a) natural fur without any treatment, (b) fur after wet chemical process, (c) fur after plasma treatment.

Significant influences of plasma pre-treatment on shoot and root seedlings growths were found. Significant differences were found in the samples treated under the 5 and 10 minutes exposition (t-test, $P<0{,}04$). The highest length of shoot, length of root and weight of root were 68 mm (121% in comparison to control sample), 101 mm (115%), and 0,224 mg (126%) respectively for pre-treatment of 10 min (see Table 1).

The increase in seedling biomass was greater in roots than in above-ground plant bodies. It also corresponds to root/shoot ratio (R/S ratio) in Figure 6. This fact may play an important role in stress conditions after sowing seed in the field.

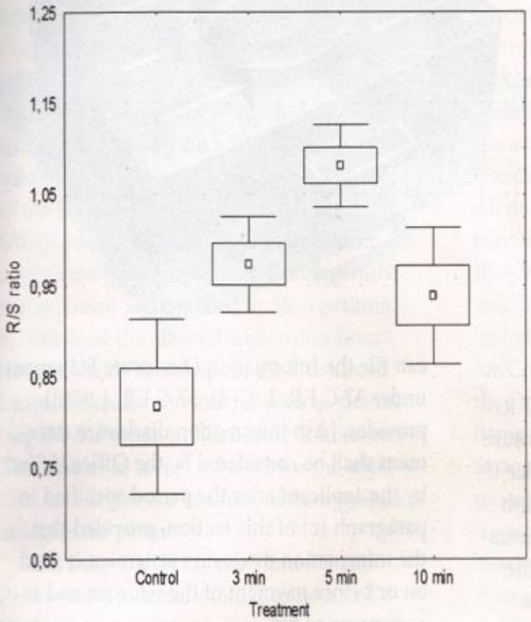

Figure 6. Root/shoot ratio of barley seedlings on the 6th day of experiment. Enhancing of the underground organ growth is evident in comparison with the control sample (0 min).

Conclusions

The gliding arc–based device is very suitable for wide range of applications. The water contact angle measurements on PE surface confirmed the possibility of device usage for surface energy enhancement. The efficiency of the process can be enhanced by water vapor addition but it is necessary to add it to the flowing plasma between electrode and treated surface.

Very interesting results were obtained in the field of rabbit fur pre-treatment for felting.

The synergy effect of simultaneous incidence of ozone, active species and UV light produced by the discharge for organic dye decomposition was proved. The dye degradation can be enhanced by presence of feasible photocatalytic layer activated by high-energetic UV light from the discharge.

The other test proved a positive effect of the gliding arc plasma pre-treatment on barley seeds.

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