LA-UR-17-22230
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Title:	Use of Atmospheric-Pressure Plasma Jet for Polymer Surface Modification: An Overview
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Intended for:	Report
Issued:	2017-03-16

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University of Oregon: Polymer Internship End-of-Term Report

Los Alamos NATIONAL LABORATORY EST. 1943

Atmospheric-Pressure Plasma Jet Polymer Treatments: An Overview

Abstract

Atmospheric-pressure plasma jets (APPJs) are playing an increasingly important role in materials processing procedures. Plasma treatment is a useful tool to modify surface properties of materials, especially polymers. Plasma reacts with polymer surfaces in numerous ways thus the type of process gas and plasma conditions must be explored for chosen substrates and materials to maximize desired properties. This report discusses plasma treatments and looks further into atmospheric-pressure plasma jets and the effects of gases and plasma conditions. Following the short literature review, a general overview of the future work and research at Los Alamos National Laboratory (LANL) is discussed.

Introduction

Polymers are best known for their low-cost, ease of manufacture, and use in a wide variety of applications, but their surface properties often need to be altered to meet demands for adhesion, friction, wettability, scratch-resistance, or biocompatibility.[1] The different methods of surface modification can be divided into four categories: mechanical, chemical, combustion, and plasma. Surface modification using plasma is an emerging field and is becoming increasing popular due to the concern of environmental pollution from alternative methods.[2]

Plasma is sometimes referred to as the fourth state of matter, but exhibits quite different properties from substances in the gaseous, liquid, or solid state. It is a highly reactive environment consisting of negatively charged electrons, highly charged positive ions, and neutral atoms or molecules. Plasma occurs naturally in lightning, Aurora Borealis, and the Sun, but has also been used extensively in industrial and technological applications, from semiconductor fabrication to discharge tubes like neon signs or florescent lights.

Plasma sources have also been used for polymerization, using plasma sources that generate a gas discharge to provide energy, initiating polymerization of a liquid monomer (that often contains a vinyl group). This process has been around since as early as the 1870's but the polymers were disregarded as an unwanted byproducts. Since the 1960's, however, it has often been used in coating processes in which a material is directly polymerized and attached to the desired surface using plasma energy.[3]

Traditionally, surface modification, such as cleaning, uses solvent-based methods, but concerns exist about health and safety and the environmental effects of volatile organic solvents, and even less hazardous chemical substitutes.[2] An important advantage of using plasma is that it is a process with minimal waste and does not require hazardous pressures. It also provides reliable and consistent results in surface activation or wetting, cleaning, and etching. Plasma sources used for surface modification include plasma torches, low-pressure plasma systems, and transferred arcs, but their uses are limited.

Treating polymers with plasma can be accomplished in a vacuum or at atmospheric pressure. Performing plasma treatments in a vacuum has several disadvantages. An atmospheric pressure plasma jet (APPJ) may be used to treat a larger range of materials and with simpler equipment. These APPJs come in the form of needles, pens, and pencils, are hand-held and manually directed.[4] This eliminates the need for an expensive vacuum system, load locks, and robotic assemblies requiring frequent maintenance. Also, the size and configuration of the object to be treated is not constrained by the dimensions of a vacuum chamber.

APPJs have many applications in diverse fields. Studies in the medical industry include the treatment of wounds without damaging tissue and treating bacteria and fungi. The plasma jet has even been proposed as a novel method for anticancer treatment, with studies being done in human breast cancer cells. Plasma treatment has been used as an antiseptic in the medical industry, and is also effective to sterilize meat surfaces. Treatment on tooth enamel was examined and found to have an effect on surface roughness and aid in tooth whitening, possibly opening up new options for dental procedures. Other areas of research include the decontamination of chemical and biological warfare agents, and deposition of silicon dioxide films.[5,6,7]

In an effort to design an effective experiment in a similar area of research, this literature review will focus primarily on the atmospheric-pressure plasma jets, their researched applications, experimental effects on various polymer surfaces and appropriate analysis methods. The final section will provide insight into the research plans and goals at Los Alamos National Laboratory.

Current State of the Technology

The simplest design of an atmospheric-pressure plasma jet, shown in Figure 1, is a dielectric tube, commonly glass, ceramic, or quartz, containing two concentric electrodes separated by a small gap[8]. A typical APPJ will operate with radio frequency of 13.56 MHz applied to the central electrode and RF power of 250 W. Though changing this power has an effect on the results, most APPJs do not have the option to alter the power level.

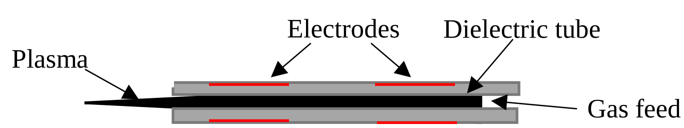

Figure 1. General plasma jet schematic.

Helium, oxygen, or other gases will flow through the tube and between the two electrodes, igniting the plasma and launching it through the outer electrode which can then be directed to a substrate downstream, sometimes up to 12 cm away.[9]

The carrier gas is used to produce a homogenous, non-thermal discharge at atmospheric pressure. Compressed air is usually used as a standard gas but it is important that this source is dry and free of contaminants. Humid or oily compressed air can negatively influence results or lifetime of the equipment. Small quantities of other gases, such as oxygen, are sometimes added to produce the chemically active species.[9]

Techniques such as chemical etching of different polymers is typically promoted by radicals such as O_2 discharges. *Hegemann et al.* conducted a surface study on the effect of various plasmas on the surface of polypropylene and it was determined that the polymer degraded under an Ar plasma, but was reinforced by cross-linking under He or N_2 discharges.[1] An etching study was conducted by *Jeong et al.* in which a O_2 /He plasma jet better etched organic materials such as Kapton whereas a CF_4/He plasma jet etched SiO_2 surfaces well.[8]

The methods used to evaluate samples ranged from surface analysis such as XPS to lap shear tests. The most common method cited in literature to test adhesive strength was a lap shear test in accordance with DIN EN 1465.[1, 8-10] A tensile testing machine is often used to provide lap shear strengths and failure modes are reported afterwards based on visual inspection. Surface roughness, topography, and chemical composition are also frequently characterized via X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM) topography.

Plasma treatments introduce unpaired electrons creating new excited states on the polymer surface, leading to an increase in surface energy and decrease in contact angle, which increases the wettability.[10] Both contact angle and surface free energy are examined to determine the wettability of the polymer surface. The higher the surface energy and smaller the contact angle, the stronger the adhesion between two surfaces.[2] Interfacial shear strength is sometimes reported from a micro bond, or pull-out, test to analyze fiber-matrix adhesion.

J. Law et al. studied the effect of pen distance to substrate, temperature, and water contact angle on surface properties. These results are summarized in Table 1.[4] *S. Tang et al.* conducted an experiment looking at the effect of the time of treatment. It appears that there is an optimal time of treatment dependent on the power and materials; too long or too short yielded larger contact angles, as shown in Table 2.[11]

Distance from material	32-22 mm	11 mm	1 mm
Temperature (°C)	30-40	55-65	140
Water contact angle (°)	70-75	10	40-10
Damage	No apparent reaction	Surface activation	Ablation

Table 1. Plasma induced thermal parameters with a composite surface conducted by J. Law et al.[4]

Treatment time (s)	0	15	35	45	60	80	100	120	150	200
Water contact angle (°)	50.5	32.7	23.2	15.5	10.3	12.9	17.5	18.4	16.4	16.3

Table 2. Effect of plasma treatment time on the contact angle of water on stainless steel conducted by S. Tang et al.[11]

All findings presented above, as well as further research not discussed, will be used when designing experiments and implementing the use of plasma jet technologies at Los Alamos National Laboratory.

Future Directions

The application of plasma pen technology will be studied at Los Alamos National Laboratory. The main goal of the experiment is to determine the optimal plasma pen parameters to promote adhesion of various substrates. In addition to an extensive literature review of similar research, numerous experiments will be conducted over the course of several months.

The PVA Tepla Plasma-Pen^{TM}, shown in Figure 2, is a hand-held plasma source which is typically used with dry compressed air as the feedstock gas, but a few other gases, to be determined, will be examined. It can be used on a wide range of materials, but the study will focus on typical materials used in laboratory applications. Some examples of these materials are laboratory produced adhesives and substrates, common epoxies and polyurethanes, aluminum, and nylon.

Figure 2. Patented atmospheric plasma system PVA Tepla Plasma-Pen^{TM}.

Using a Design of Experiment and the JMP software, different factors and corresponding levels will be studied to maximize various responses. Factors may include type of gas, the adhesive, the substrate, plasma pen tip, time of exposure, aging time after exposure and before adhesion, and the distance of pen tip from substrate.

Responses that will be analyzed are still to be determined but may include results from testing using an MTS Insight 30 such as lap shear adhesive strength and failure modes and contact angle measurements from a drop shape analyzer.

Although the plasma pen has previously been used at the laboratory, its operational parameters have not be studied and is not often incorporated into research. The pen has been used minimally for the removal of films, repairing of epoxies, and adhering materials. An experiment designed to determine optimal use parameters will provide information that will allow scientists and engineers to use this tool with confidence to achieve optimal adhesion in a variety of applications.

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