Atmospheric Pressure Plasma Treatment of Polymers

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Atmospheric Pressure Plasma Treatment of Polymers

Relevance to Adhesion

Edited by

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Front cover illustration shows surface functionalization of three-dimensional polymer substrates using AC corona discharge at atmospheric pressure.

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Preface

Polymeric materials are used for a legion of applications in a host of technological areas. However, polymers are innately hydrophobic, low surface energy materials and thus do not adhere well to other materials brought in contact. This necessitates their surface modification/treatment/activation to render them adhesionable. Apropos, surface modification is carried out not only to improve their adhesion characteristics but for a variety of other reasons too, for example to increase their hydrophilicity or hydrophobicity, to modify their tribological behavior, to render them flame resistant, etc.

A plethora of techniques (ranging from vacuum to atmospheric-pressure, wet to dry, simple to sophisticated, and inexpensive to sumptuous) have been employed to attain the required functional characteristics of polymers. Low-pressure (vacuum) plasma has been used for quite some time for polymer surface modification, but in the past decade there has been explosive growth of interest in atmospheric-pressure plasma (APP) processes because of their technological and economic advantages. They require no vacuum, need no expensive equipment, are easy to handle, can be used in a continuous mode, have a very good scalability, and can be simply integrated in existing process lines. Concomitantly, APP technology has been effectively utilized to treat polymers, paper, rubber, wool, fabrics, steel, glass and fiber-reinforced composites. Also, there has been much activity in ameliorating the existing processes, plasma sources and reactors or in devising new and improved ways to implement APP technology.

Besides plasma-based surface modification (activation, functionalization) using a number of gases, researchers have also been working on coating processes using atmospheric-pressure plasmas. Three different kinds of processes for coating deposition using atmospheric-pressure plasmas are being actively pursued. First is the grafting process where, after suitable plasma activation of the surface, the monomer is coupled on the surface using a subsequent wet-chemical step or gas-phase reaction. The second process is aerosol-based in which the precursor is directly sprayed into the plasma zone. The third kind of process is the plasma enhanced chemical vapor deposition (PECVD) in which a precursor, frequently together with a suitable process gas, is introduced into the discharge. It should be mentioned that besides the dielectric barrier discharge (DBD), other plasma sources (e.g., surface barrier discharge (SBD), coplanar barrier discharge (CBD), plasma jets, AC corona discharges, etc.) working at atmospheric pressure are of great interest.

Now coming to this book (containing 15 invited articles) it is divided into two parts:

Part 1: Fundamental Aspects and

Part 2: Adhesion Enhancement.

Topics covered include: combinatorial plasma-based surface modification of polymers; treatment of polymer surfaces with surface dielectric barrier discharge plasmas; selective substitution reactions on polymer surfaces by different plasmas; dielectric barrier discharge pretreatment of polymers in presence of aerosols; nanoscale surface structures on wool fabrics by atmospheric-pressure plasma treatment; nanosilica coatings on plasma activated polymers; biomedical applications of atmospheric plasma treatment of polymers; atmospheric-pressure plasma polymerization surface treatments for enhanced polymer-polymer and metal-polymer adhesion; functionalization and adhesion enhancement of various polymers using atmospheric pressure plasmas; atmospheric plasma treatment in extrusion coating; and enhancement of fracture toughness of adhesively bonded systems using atmospheric-pressure plasma treatment.

It should be recorded that all manuscripts were rigorously peer-reviewed, properly edited and suitably revised (some twice or thrice) before inclusion in this book.

This book representing the cumulative wisdom of a number of key researchers provides an overview and highlights the latest developments in APP technology. The book should be of much value to anyone interested in harnessing the potential of APP technology in enhancing adhesion in a variety of industries, namely printing, packaging, aerospace, automotive, composites, microelectronics, biological and biomedical, and others. As we delve further into the working of APP technology, new application vistas will emerge. This covers the large area treatment, e.g. internal coating of closed polymer bags or microfluidic devices and microplasmas for area-selective treatment of polymers. Moreover, treatment of skin for wound dressing is a very promising technology, which is under investigation and could be introduced into the market soon.

As a side comment, APP sources find their way into household applications. Kash Mittal has even heard that a company is planning to come up with an APP device for *in-situ* treatment of lips to enhance lipstick adhesion and of nails to enhance nail polish adhesion. What an interesting and exciting application!

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PART 1

FUNDAMENTAL ASPECTS

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Combinatorial Plasma-based Surface Modification of Polymers by Means of Plasma Printing with Gas-Carrying Plasma Stamps at Ambient Pressure

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Abstract

In this work a new method of achieving combinatorial area-selective modification of polymer surfaces is presented, utilizing atmospheric-pressure plasma printing with novel gas permeable electrodes. In these "plasma stamps" a microporous gas-carrying layer provides exchange of gaseous species from the gas stream to the individual microcavity discharges. Additionally, the electrodes can be fed with two (or more) different gases from spatially separate locations, allowing the generation of spot arrays with controlled gradients of physicochemical surface properties. Plasma-printed gradient surfaces can be used for combinatorial studies, for example in biomedical or polymer electronic research. In combination with spatially resolved surface characterization methods, the investigation of plasma-surface interaction processes can be significantly simplified. In the present contribution, gradient spot arrays were applied to optimize gas composition and functionalization parameters to provide optimal nucleation and growth of an electroless metal coating on a polymeric substrate. Locally plasma-modified surfaces were quantitatively

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characterized applying chemical derivatization (CD) followed by FTIR-ATR or SEM-EDX analyses in order to determine the area densities and spatial distributions of functional groups which are reactive towards the derivatization reagents used. Two chemical derivatization techniques were utilized: gas-phase derivatization (i) with 4-(trifluoromethyl)benzaldehyde (TFBA), forming a stable Schiff base with primary – but not secondary – amino groups, and (ii) with 4-(trifluoromethyl)phenyl isothiocyanate (TFMPITC) which is able to react with both primary and secondary amino groups forming thioureas, but – under the conditions used – not hydroxyl groups. It was, however, recently pointed out by us that other nitrogen-bearing functional groups such as imines can be captured by these methods as well.

Keywords: Dielectric barrier discharges, plasma printing, microplasmas, porous plasma stamps, polymer surface modification, gradient arrays, combinatorial plasma chemistry

1.1 Introduction

The term "plasma printing" stands for patterned surface modification or plasma-enhanced film deposition using ambient-pressure microplasmas enclosed in sub-millimeter sized cavities [1]. In early investigations, ceramic plates with laser- or mechanically drilled cylindrical through-holes covered by a fine metal mesh were used in order to allow diffusive gas exchange between the cavities and ambient. The mesh simultaneously served as one of two discharge electrodes, providing the electric field necessary to ignite a barrier discharge within the cavity. Using such an arrangement, the process gas can be transported by a stagnant flow and diffuse through the mesh into the cavities below it, enabling surface treatment with larger amounts of gas than available in the enclosed cavity volume. Different kinds of thin films with thicknesses up to several 100 nm have been deposited with arrangements of this kind [2, 3].

Producing more complicated patterns or larger arrays of regular vias in ceramic plates by laser-based or mechanical methods, however, is not trivial. Using free-standing insulator sheets for the definition of the plasma-printed areas, it is generally impossible to generate patterns in which the non-treated areas are not connected. In addition, a good mechanical contact between the plasma stamp and the substrate to be treated cannot be easily guaranteed because the application of uniformly distributed mechanical forces interferes with the provision of a stagnant gas flow over an area of several square centimeters.

For these reasons, recent work on plasma printing has focused on "plasma stamps" with closed cavities, produced by photolithographic techniques or by electromagnetic engraving [4] which were used for patterned plasma nitrogenation[1] or plasma oxidation of polymer surfaces with lateral dimensions on the order of 100 µm or lower.

In order to make the patterned deposition of thicker coatings using plasma printing feasible, new solutions are required for the assembly of dimensionally stable plasma stamps that provide an exchange of gaseous species with the discharge in the cavity. Interesting opportunities are afforded by utilizing recent developments in the field of porous metallic materials, such as components with high permeability and porosity, which can be obtained from the sintering of metal fibers [6].

The principle of plasma stamps with a porous gas-carrying layer is illustrated in Figure 1.1. Compared with closed versions of plasma stamps the new design utilizing a microporous gas-carrying layer as an electrode offers a number of advantages:

- If surfaces shall not only be modified, like in the present paper, but when thin films beyond a few nm thickness are to be deposited, gas-carrying plasma stamps are a big advantage because virtually unlimited gas volumes can be fed into the micro-cavities and can be used for film formation.
- The cavities formed by the substrate and the stamp can be fed with the gas quite rapidly and very sparingly. Oxygen traces in the cavities can be quickly displaced while getting around the necessity to provide an oxygen-free environment. This point is very important if polymer surfaces are to be plasma-nitrogenated because oxygen molecules compete with intermediate radical centers in this process [7].
- During the plasma treatment or coating of a surface, typically lasting a few seconds, a time-independent

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[1] In view of the fact that imines will probably also react with most of the derivatization and labeling reagents generally used for amine detection and quantification [5], we use this expression instead of "plasma amination."