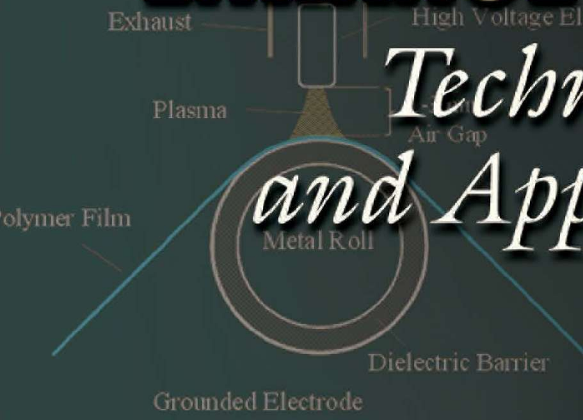
Adhesion and Adhesives: Fundamental and Applied Aspects

POLYMER SURFACE MODIFICATION TO ENHANCE ADHESION

Techniques and Applications



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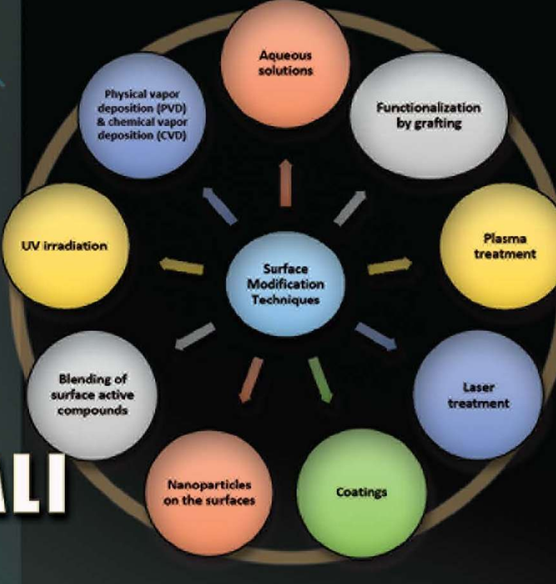

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Polymer Surface Modification to Enhance Adhesion

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100 Cummings Center, Suite 541J
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The topics to be covered include, but not limited to, basic and theoretical aspects of adhesion; modeling of adhesion phenomena; mechanisms of adhesion; surface and interfacial analysis and characterization; unraveling of events at interfaces; characterization of interphases; adhesion of thin films and coatings; adhesion aspects in reinforced composites; formation, characterization and durability of adhesive joints; surface preparation methods; polymer surface modification; biological adhesion; particle adhesion; adhesion of metallized plastics; adhesion of diamond-like films; adhesion promoters; contact angle, wettability and adhesion; superhydrophobicity and superhydrophilicity. With regards to adhesives, the Series will include, but not limited to, green adhesives; novel and high-performance adhesives; and medical adhesive applications.

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This edition first published 2024 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA
and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA
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Library of Congress Cataloging-in-Publication Data

ISBN 978-1-394-23100-3

Cover image: Pixabay.Com
Cover design by Russell Richardson

Set in size of 11pt and Minion Pro by Manila Typesetting Company, Makati, Philippines

Printed in the USA

10 9 8 7 6 5 4 3 2 1

Contents

Preface

Polymers are used vastly in many industries for a variety of applications. However, their surfaces are intrinsically non-reactive due to their low surface free energy and absence of reactive chemical groups. Concomitantly, their surface modification (also known as surface treatment or surface activation) is a *sine qua non* to render them adhesionable or bondable.

Even a cursory look at the literature will evince that there is tremendous research activity in devising new and improved ways of ameliorating the existing techniques or coming up with novel ways to modify polymer surfaces. A legion of techniques ranging from mundane to sophisticated, vacuum to non-vacuum, dry to wet, and inexpensive to sumptuous have been documented for surface modification of a variety of polymer surfaces. The choice for an optimum technique depends on a host of factors, *inter alia*, the chemical structure of the polymer substrate, nature of mating phase, level of adhesion desired and cost. Also, the longevity of treatment is a very significant consideration. There have been different attempts to prolong the life of treatment as well.

The information on the topic of this book is scattered in many different publication media and there is no single, easily accessible, and comprehensive source available. This lacuna in the literature provides the vindication and motivation for bringing out this book.

This book containing 13 (a lucky number) chapters is divided into two parts: Part I: Energetic Treatments; and Part II: Chemical Treatments. Topics covered include: atmospheric pressure plasma treatment of polymers to enhance adhesion; corona treatment of polymer surfaces to enhance adhesion; flame surface treatment of polymers to enhance adhesion; vacuum UV photo-oxidation of polymer surfaces to enhance adhesion; optimization of adhesion of polymers using photochemical surface modification; UV/Ozone surface treatment of polymers to enhance adhesion; adhesion enhancement of polymer surfaces by ion beam treatment; polymer surface modification by charged particles; laser surface modification of polymeric materials; competition in adhesion between polysort and monosort functionalized polyolefinic surfaces; amine-terminated dendritic materials for polymer surface modification;arginine-glycine-aspartic acid (RGD) modification of polymer surfaces; and adhesion promoters for polymer surfaces.

The chapters are written by renowned researchers actively engaged in surface modification of polymers. This book is profusely referenced and copiously illustrated.

This book should of great appeal and interest to polymer scientists, surface scientists, adhesionists, materials scientists, plastics engineers, and to those involved/interested in adhesive bonding, packaging, printing, painting, metallization, biological adhesion, biomedical devices, and polymer composites.

Now it gives us great pleasure to acknowledge all those who played essential roles in giving this book a body form. Naturally, first and foremost, our profound thanks go to the authors for their keen interest, sustained enthusiasm, unwavering cooperation, and sharing their valuable research experience in the form of written accounts (which essentially provided the grist for this book), without which this book could not be materialized. Also, the steadfast interest and whole-hearted support of Martin Scrivener (publisher) in this book endeavor is highly appreciated.

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Part I

ENERGETIC TREATMENTS

1

Atmospheric Pressure Plasma Treatment of Polymers to Enhance Adhesion

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Abstract

In this chapter, we present an overview on recent research and development work in the area of atmospheric pressure plasma treatments (APPTs) to generate adhesion-promoting surfaces of polymers used in various applications in automotive, aerospace, packaging, and medical fields. In comparison to the classical "corona treatment" the APPTs provide access to a broader range of industrially interesting surface modifications that are normally better controlled with respect to their physicochemical nature. Thus, application of APPTs may become a superior option for preparing polymer surfaces for adhesive bonding, adhesive-free low-temperature bonding involving homogeneous and heterogeneous substrates, lacquering, or coupling of specific biomolecules, proteins, or cells. APPT technology is, however, not only flexible for tuning surface chemistry but also is flexible with respect to plasma source and equipment design. Versatility of the APPT technology facilitates its integration into a variety of process chains. An example presented here is a hybrid technology combining both APPT and additive manufacturing based on 3D printing processes using fused filament deposition. Inline treatment by quasi-simultaneous execution of printing and APPT can, for instance, increase the adhesion of 3D printed products in print direction (z-Axis) and thus increase the mechanical stability of the printed part. In the medical field such a technology may be attractive for cell growth by promoting treatment of internal surfaces of printed porous scaffolds. In future, products made from bio-based or recycled polymers will become increasingly important. APPT technology could become an important enabler for meeting the technical requirements for the adhesion of such products.

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K.L. Mittal and A.N. Netravali (eds.) Polymer Surface Modification to Enhance Adhesion: Techniques and Applications, (3–44) © 2024 Scrivener Publishing LLC

Keywords: Atmospheric pressure plasma treatment, chemical groups, functional coatings, bonding, adhesive-free bonding, additive manufacturing, binding of biomolecules

1.1 Introduction

Polymers play an important role in packaging, automotive, medical, biomedical, and aerospace applications. Polymer market still experiences growth, driven by the increased use of polyolefins and also of new bio-based and functional polymers. Most of these polymers exhibit inert surfaces that need to be treated to provide sufficient adhesion for lacquers, paints, and adhesive bonding. Treatment can be carried out using a wide range of surface-functionalizing processes including wet-chemical etching [1, 2], plasma [3–5], and laser modification [4, 6, 7], as well as ozone and UV treatment [4], many of which are nowadays well established in industry. In recent years, application of cold Atmospheric Pressure Plasma Treatments (APPTs) in industry has experienced very strong growth attributed to the high versatility in applications, low investment cost and the very good integration of the technology in existing process chains [8].

Changes in technical, social, and legal requirements will inevitably lead to changes in processes also in the adhesive bonding industry which are therefore the focus of this review. Adhesive bonding technology is used in a wide range of products as it offers various material combinations, long-term stability and safety while maintaining material properties and creating additional functions in the bonded product. Continuous inventions and innovations in the development of raw materials, adhesives and bonded products have enabled a dynamic development in the past decades.

Innovative bonding technology enables new, more environmentally-friendly and sustainable products and processes in many areas. For instance, improved resource efficiency can be achieved in the production of renewable energy power plant components where sealing of solar cells or joining of wind turbine rotor blades has become possible. Another example is the electromobility area with the sealing of battery cells, heat management of batteries with heat-conducting adhesives and hermetic sealing of fuel cells. In addition, adhesives with improved product properties can lead to savings, even in food packaging to increase shelf-life with resource-efficient materials.

In Europe the “European Green Deal” with its agenda responding to current socio-political changes will bring additional requirements and thus new challenges for bonding technology [9, 10]. The main point is the transition from a linear to a circular economy, minimizing the use of resources, generation of waste and emissions, and the inefficient use of energy. This will be achieved by considering resource needs, life extension, repair, refurbishment, recycling and closing energy and material loops.

The eco-friendly APPT technology with its innovations in combining suitably functionalized surfaces with bonding technology certainly has the potential to meet the new set of requirements that may result from implementation of the agenda of the European Green Deal.

These new challenges must be realized in terms of closed-loop systems along the value chain. Therefore, life cycle assessments (LCAs) enable a holistic view of adhesively bonded products with regard to ecological and economical improvements along the complete value chains [11, 12]. In this context atmospheric pressure plasma treatments (APPTs) of polymers and other materials like paper, rubber, fabrics, steel, glass and different composite materials have gained considerable importance in recent years due to their technological and economical capabilities and thus offer the potential to become the future leading technology for surface functionalization to improve adhesive bonding technology. The main advantages of APPTs are that they need no expensive equipment, are easy to handle, have a very good scalability and can simply be integrated in existing process lines.

Considering that in most applications materials are joined with other structural parts, the adhesion behavior is of great significance. The adhesion property is strongly affected by the chemistry and morphology of the surfaces. APPTs alter surface morphologies and chemical composition of different materials without affecting their bulk properties. The plasma treatment can also change the surface from hydrophobic to hydrophilic state and vice versa, depending on the type of monomer or process gas used for surface activation. Thus, plasma treatment can alter the inert polymer surface to have greater chemical/physical affinity by incorporating chemical functional groups. This leads to an increase in surface free energy and enlargement of the contact area and thus improved adhesion property. Different research groups have carried out a variety of APPT processes to improve the surface properties of materials [13–19].

These cold plasma treatments have gained increasing interest as they represent environmentally-friendly solution and can even be performed under atmospheric pressure conditions at relatively low cost [20–22]. The plasma treatment can also affect the morphology by exerting the etching effect on the surface and changing the surface roughness and wettability. This results in improved adhesion of metal/plastic compounds [23]. The cold plasma treatment of various plastics such as polypropylene, polyethylene, poly(ethylene terephthalate), poly(etheretherketone), etc. has been investigated [24–26].

In this chapter, we will focus on the use of APPTs to improve the adhesion by chemical functionalization for different applications. Firstly, we will give a short overview about the historical development of APPTs. The second section is about the establishment of functional surfaces with a high number of different chemical groups. In the third section, the adhesion improvement by APPT promoted joining of materials is discussed. In the fourth section we will show the relevance of APPTs for biomedical application for improving e.g. cell adhesion. Finally, we will give an overview on the use of APPTs to promote adhesion in additive manufacturing processes.

1.2 Historical Development of APPTs

The industrialization of APPTs started in 1951, when A. W. Eisby, a Danish engineer, invented a high-frequency treatment with a dielectric barrier discharge in air for polymer foils to improve the adhesion of inks [27]. This so-called "corona treatment" is nowadays commercially well established in the packaging sector for surface activation and cleaning. In the following decades different kinds of plasma sources for APPT working with air as process gas were developed, enabling the treatment of flat and complex surfaces [5]. In the meanwhile, APPTs have been established in the biological, pharmaceutical and medical fields, in automotive, aerospace, and electronics industries and have become important for the alternative energy sector, additive manufacturing as well as for the pretreatment of renewable and sustainable materials. Figure 1.1 shows the most common sources like dielectric barrier discharges, stabilized corona systems, and plasma jets or torches which can be operated using different types of excitations, e.g., alternating current (AC), pulsed direct current (DC), low-frequency (kHz), radio frequency (RF, 13.56 MHz) and microwaves (MW) with a frequency of 2.45 GHz.

Today APPTs can be used to functionalize a surface with various chemical groups including e.g. -OH, -COOH, $-NH_2$, $-NO_x$ to improve the adhesion of, e.g., adhesives, lacquers and paints to polymers. Using nitrogen and nitrogen-hydrogen mixtures as process gases, for example, imines, amines or amides can be introduced on the polymer surface, frequently leading to higher surface free energy, better long-term stability and in many applications the desired high level of adhesion. DBD-based APPT using nitrogen or its mixtures with other gases like

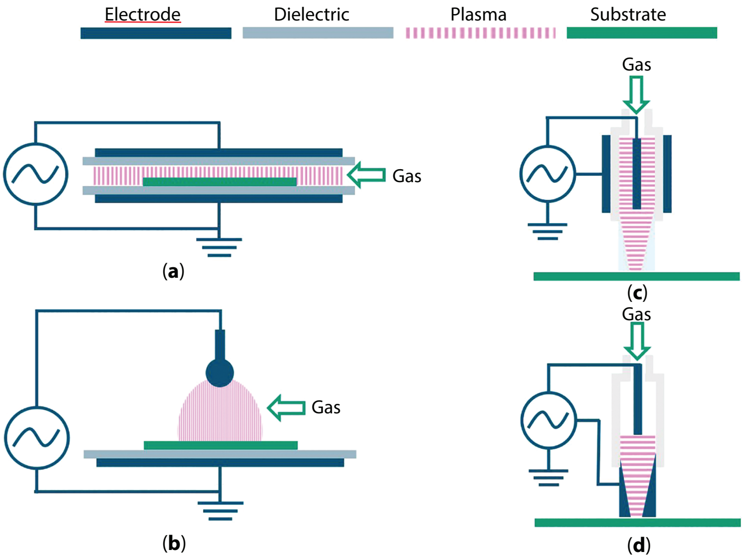

Figure 1.1 Examples of different types of plasma sources for APPTs; (a) Dielectric Barrier Discharge (DBD), (b) Stabilized Corona, (c) DBD jet, and (d) Arc jet.

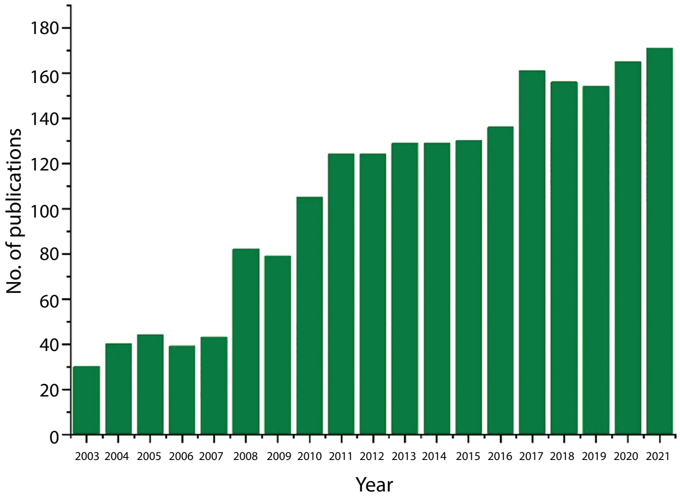

Figure 1.2 Number of publications on surface functionalization with APPT with relevance to adhesion (from Web of Science – date Nov. 15, 2022).

hydrogen as process gas are in the meanwhile commercially available on the market and have been recognized as a very good alternative to existing wet-chemical etching processes.

In the last decades an increasing number of leading research groups have worked on the topic of adhesion-promoting surface modifications for coating processes with atmospheric-pressure plasmas. Depending on the precursors and processes used, they have demonstrated that high densities of chemical functionalities such as alcohols, epoxides, amines, carboxylates or silanols can be obtained on the surface. Current statistics of publications as available via the website from "Web of Science" for surface functionalization using APPTs with relevance to adhesion is shown in Figure 1.2. With presently 170 publications per year this number has increased fivefold compared to 2003.

1.3 Functional Groups Produced by APPTs

Depending on the atmospheric pressure plasma system used, process gases, precursors and process parameters, the surfaces of several materials can be cleaned, activated or equipped with a wide range of functional layers.

Figure 1.3 shows the generated chemical species by a microdischarge in air of a dielectric barrier discharge (DBD), which has been modelled by Eliasson and Kogelschatz [28]. The predominant species are electrons, ionized species, free radicals, ozone and NO_x as well as UV light.

They have shown that the composition of species present varies depending on the timescale within a microdischarge of a DBD. On a nanosecond scale radicals and excited oxygen and nitrogen are dominant, whereas on a microsecond scale mostly ozone, NO_x and excited nitrogen are present. In the scale of seconds, ozone and also N_2O are the dominant species.

Compared to a cold DBD at room temperature, arc torches have higher temperatures of more than 600°C. At this high temperature the concentration of NO_x species will increase strongly and thus lead to different surface chemistry.

With the aforementioned reactive species organic contaminants, generally present on the surface, can be decomposed and removed. At the same time the surface becomes activated by formation of functional moieties such as nitrogen- and oxygen-containing groups. This leads to significant changes in the chemical composition of the topmost layer and thus in the surface free energy of the treated polymer. Direct electrical charging of the polymer surface by trapping ions by CH_2 groups of the polymer can also contribute to the increase of surface free energy [29].

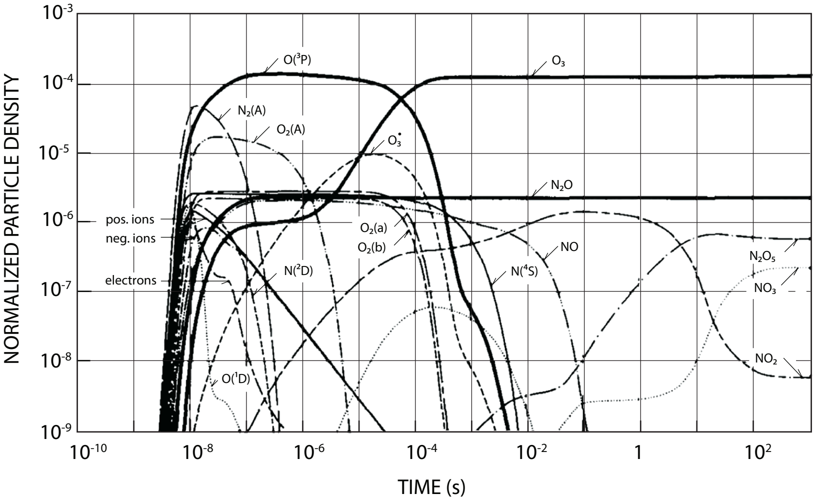

Figure 1.3 Chemical species generated by a microdischarge in air (from [28]).

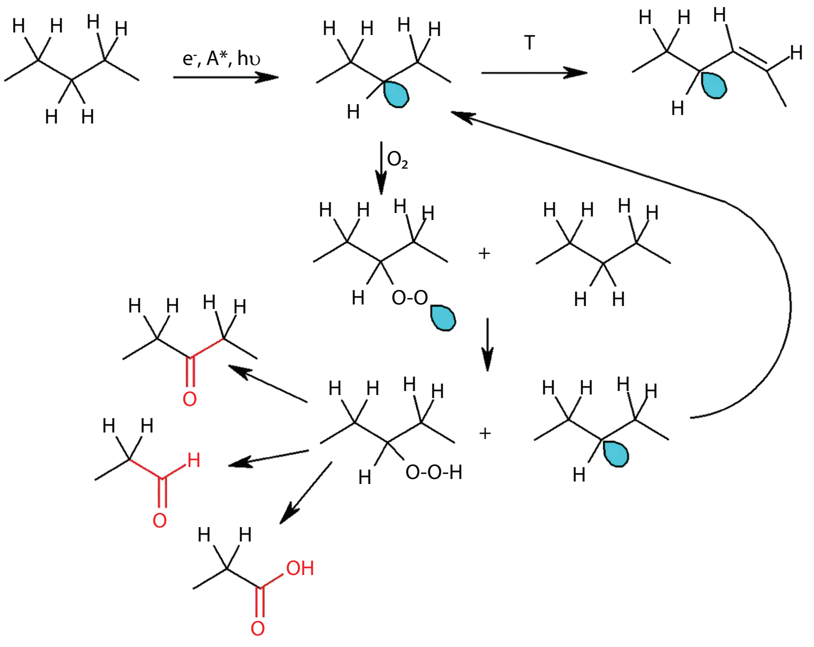

Figure 1.4 Important reaction steps for the activation of polypropylene surface (adapted from [30]).

In general, the surface free energy can be increased by atmospheric plasma treatment. A basic model for polypropylene was described by Dorai and Kushner and is presented in Figure 1.4 [30].

The first step is the formation of alkyl radicals which can also transform into allyl radicals. The next step is the formation of peroxide radicals by the reaction of the alkyl radicals with oxygen (diradical). The peroxide radicals abstract hydrogen from other alkyl groups and this leads to formation of new alkyl radicals. The hydroperoxides formed can react to form various stable oxygen functionalities like aldehydes, ketones or carboxylates, resulting in "active" surfaces and increased surface free energy and in many cases, this leads to an improved adhesion.

In general, the enhancement of the bonding quality is highly dependent on the material, the type of APPT system and treatment conditions used. An interesting example for future use of sustainable materials is the plasma treatment of wood. Solvent- and water-based polyurethane (PU) coatings showed deeper penetration in pre-treated wood in comparison to untreated wood substrates [31].

1.3.1 Nitrogen-Based Surface Modification

In addition to the classic "plasma pretreatment" of surfaces in air routinely used today, more and more processes with a defined oxygen-free (inert) gas atmosphere are becoming relevant. Such a defined atmosphere is necessary to establish specific chemical groups on the surface of the material and to avoid the influence of reactive oxygen groups. The easiest way is the use of nitrogen or nitrogen-hydrogen (forming gas) mixtures as process gas. Figure 1.5 shows possible functional groups on polypropylene surface generated by corona treatment and APPT using nitrogen/hydrogen as process gas. For example, when treating polypropylene with nitrogen or nitrogen/hydrogen mixtures, a relatively high density of N-containing reactive groups such as imines or amines can be generated on the surface [5, 32, 33].

In investigations studying the treatment of polypropylene surfaces with an AC Corona System stabilized by a dielectric barrier (RotoTEC, Tantec A/S, Denmark) it was found that using nitrogen and especially nitrogen-hydrogen mixtures higher surface free energy levels could be reached compared with classical air treatment and are presented in Figure 1.6. This indicates a difference in the types of surface compositions in these two cases. Further, surface free energy changes achieved with the N_2/H_2 mixtures were observed to be stable over a period of several weeks [34]. Moreover, in the case of adding hydrogen a long-term stability of the surface free energy for several weeks was shown.