Adhesion and Adhesives:

Fundamental and Applied Aspects

Atmospheric Pressure Plasma Treatment of Polymers

Relevance to Adhesion

Edited by Michael Thomas and K.L. Mittal



WILEY

Atmospheric Pressure Plasma Treatment of Polymers

Relevance to Adhesion

Edited by

Michael Thomas and K.L. Mittal



WILEY

Copyright © 2013 by Scrivener Publishing LLC. All rights reserved.

Co-published by John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts.

Published simultaneously in Canada.

No part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, scanning, or otherwise, except as permitted under Section 107 or 108 of the 1976 United States Copyright Act, without either the prior written permission of the Publisher, or authorization through payment of the appropriate per-copy fee to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, (978) 750-8400, fax (978) 750-4470, or on the web at www.copyright.com. Requests to the Publisher for permission should be addressed to the Permissions Department, John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, (201) 748-6011, fax (201) 748-6008, or online at http://www.wiley.com/go/permission.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives or written sales materials. The advice and strategies contained herein may not be suitable for your situation. You should consult with a professional where appropriate. Neither the publisher nor author shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

For general information on our other products and services or for technical support, please contact our Customer Care Department within the United States at (800) 762-2974, outside the United States at (317) 572-3993 or fax (317) 572-4002.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic formats. For more information about Wiley products, visit our web site at www.wiley.com.

For more information about Scrivener products please visit www.scrivenerpublishing.com.

Cover design by Russell Richardson

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

Library of Congress Cataloging-in-Publication Data:

ISBN 978-1-118-59621-0

Printed in the United States of America

Atmospheric Pressure Plasma Treatment of Polymers

Scrivener Publishing

100 Cummings Center, Suite 541J Beverly, MA 01915-6106

Adhesion and Adhesives: Fundamental and Applied Aspects

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.

Series Editor: Dr. K.L. Mittal 1983 Route 52, P.O.1280, Hopewell Junction, NY 12533, USA Email: usharmittal@optimum.net

Publishers at Scrivener
Martin Scrivener (martin@scrivenerpublishing.com)
Phillip Carmical (pcarmical@scrivenerpublishing.com)

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 atmosphericpressure, 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 peerreviewed, 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!

Acknowledgements

First of all we would like to express our sincere thanks to the authors for their contribution, interest, enthusiasm and cooperation without which this book would not have seen the light of day. Second, we are very thankful to the unsung heroes (reviewers) for their invaluable comments which definitely improved the quality of these articles. Michael Thomas would like to express his thanks to Prof. Claus-Peter Klages for supporting this book project. Last, but not least, our appreciation goes to Martin Scrivener (Scrivener Publishing) for his earnest interest and important role in materializing this book.

Michael Thomas
Fraunhofer Institute for Surface Engineering
and Thin Film IST, Germany
E-mail: michael.thomas@ist.fraunhofer.de
and
K.L. Mittal
Hopewell Junction, NY, USA
E-mail: UshaRMittal@optimum. net

Contents

	efac kno		gements	xiii xvii
Pa	rt 1:	Fun	damental Aspects	1
1	Poly Gas-	mers b Carryi a Hinz	orial Plasma-based Surface Modification of by Means of Plasma Printing with ng Plasma Stamps at Ambient Pressure ze, Andrew Marchesseault, Stephanus ch, Michael Thomas and Claus-Peter Klages	3
	1.1	0	luction	4
	1.2		imental	7
		1	Porous Plasma Stamp Design and Fabrication	7
			Plasma Printing	10
			Chemical Derivatization of Functional Groups	12
			FTIR and EDX Analyses	14
		1.2.5	Electroless Metallization	16
		1.2.6	Numerical Simulation of Concentration	
			Distributions	17
	1.3	Resul	ts and Discussion	18
	1.4	Concl	usions	23
	Ack	nowled	dgements	23
	Refe	erences		24
2	Trea	tment	of Polymer Surfaces with Surface	
	Die	lectric l	Barrier Discharge Plasmas	27
	Ma	rcel Šir	nor and Yves Creyghton	
	2.1	Introd	luction	28
	2.2	A Ger	neral Overview of Surface Modification	
		Resul	ts Obtained with Surface DBDs	32
		2.2.1	Activation Processing	33
		2.2.2	Post-Activation Processing	36
				V

vi Contents

2.3	An Ov	verview of Selected Results Obtained			
	at TNO	O by the SBD	41		
	2.3.1	Hydrophilization of Polyester Fabric	41		
	2.3.2	Improvement of Adhesion of			
		Poly(vinyl chloride) and Polyurethane			
		Coatings to PET Fabric	46		
	2.3.3	Plasma-Assisted Grafting of			
		Biocidal Non-leaching Coatings	50		
	2.3.4	Hydrophobization of Cotton Woven and			
		Glass Fibre Nonwoven Fabrics	54		
	2.3.5	Corrosion-Protective Coatings of			
		Thin Aluminium Layer	59		
	2.3.6	Plasma Polymerization of Nanocomposites	62		
	2.3.7	Plasma-Assisted Self-Assembly Technique	66		
2.4	Concl	usions	73		
Refe	rences		74		
Sub	stitutio	by Atmospheric-Pressure Plasmas: Selective on Reactions on Polymer Surfaces of Plasmas	83		
	ihiro In				
3.1	Introd	S	84		
3.2	Deflu	efluorination of Poly(tetrafluoroethylene) Surfaces			
	3.2.1	Hydrophilic Modification of			
		Poly(tetrafluoroethylene) Surfaces			
		by Low-Pressure Plasma	86		
	3.2.2	Hydrophilic Modification of			
		Poly(tetrafluoroethylene) by			
		Atmospheric-Pressure Plasma	91		
3.3		ive Modification of Polymeric Surfaces			
	by Pla		102		
	3.3.1	Selective Modification with Primary Amino	101		
	222	Groups by Low-Pressure Plasma	104		
	3.3.2	Selective Modification Using	111		
	222	Bromoform Plasma	111		
	3.3.3	Direct Amination Using Atmospheric-Pressure Plasma	115		
3.4	Sumn		115 120		
	rences	nui y	121		
TICIC	rerences				

4	Pern	nanenc	e of Functional Groups at Polyolefin			
	Surf	aces In	troduced by Dielectric Barrier	131		
	Discharge Pretreatment in Presence of Aerosols					
	R. Mix, J. F. Friedrich and N. Inagaki					
	4.1	1				
	4.2	Exper	imental	135		
		4.2.1	Materials	135		
		4.2.2	DBD Treatment System	135		
		4.2.3	Analytical Characterization	136		
	4.3	Result	ts	137		
		4.3.1	Plasma-Induced Changes in Composition			
			of Surface Layer	137		
		4.3.2	Stability of Surface Modification	143		
		4.3.3	Angle-Resolved XPS Measurements	148		
	4.4	Discu	ssion	151		
	4.5	Sumn	nary	153		
	Ack	nowleg	gdements	153		
		erences		153		
5	Ach	ieving	Nano-scale Surface Structure on Wool			
	Fabric by Atmospheric Pressure Plasma Treatment					
	C.W. Kan, W.Y.I. Tsoi, C.W.M. Yuen, T.M. Choi and					
		Tang				
	5.1	O	duction	158		
	5.2	Exper	rimental	159		
		5.2.1		159		
			Characterisation	160		
	5.3	Resul	ts and Discussion	160		
			Surface Topographical Modification	161		
			Surface Wetting Behaviour	162		
		5.3.3		163		
	5.4	Conc	lusions	171		
	Ack	nowle	dgements	171		
		erences		172		
6	Det	ositio	n of Nanosilica Coatings on Plasma Activated			
			ene Films	175		
		D. D. Pappas, A. A. Bujanda, J. A. Orlicki, J. D. Demaree,				
	J. K. Hirvonen, R. E. Jensen and S. H. McKnight					
	6.1		duction	175		
	6.2	Expe	rimental	17		

viii Contents

	6.3	Resul	ts and Discussion	1/9
		6.3.1	Plasma Treatment and Surface Characterization	
			of Polyethylene Films	181
		6.3.2	Silica Synthesis and Coating of Plasma	
			Treated Polyethylene Films	186
	6.4	Concl	lusions	194
	Ack	nowled	dgement	194
	Refe	erences		195
7	Atm	osphe	ric Plasma Treatment of Polymers for	
	Bior	medica	l Applications	199
	N. C	Gomath	ni, A. K. Chanda and S. Neogi	
	7.1		duction	199
	7.2	Plasm	na for Materials Processing	200
	7.3	Atmo	spheric Plasma Sources	202
		7.3.1	Corona Discharges	202
		7.3.2	Dielectric Barrier Discharges	203
		7.3.3	Atmospheric Pressure Plasma Jets	204
		7.3.4	Microwave (MW) Driven Plasmas	204
	7.4	Effect	s of Plasma on Polymer Surface	206
		7.4.1	Plasma Surface Modification	206
		7.4.2	Plasma-Induced Grafting	207
		7.4.3	Plasma Polymerization	207
	7.5	Atmo	spheric Plasma in Biomedical	
		Appli	cations	208
		7.5.1	Plasma Surface Modification	
			of Biomaterials	208
		7.5.2	Inactivation of Microorganisms	211
	7.6	Concl	lusion	212
	Refe	erences	ł	212
Pa	rt 2	Adł	nesion Enhancement	217
ð		•	ric Pressure Plasma Polymerization Surface	
			s by Dielectric Barrier Discharge for Enhanced	
			olymer and Metal-Polymer Adhesion	219
		-	Moreno-Couranjou, Nicolas D. Boscher, David	
			my Maurau, Elodie Lecoq and Patrick Choque	
	8.1		duction	220
	8.2	Atmo	spheric Plasma Polymerization Processes	221

	8.3	Atmo	spheric Plasma Surface Modification for				
		Enhar	nced Adhesion	223			
		8.3.1	Tailoring the Surface Morphology by an				
			Atmospheric Plasma Treatment	223			
		8.3.2	Deposition of Thin Organic Layers with				
			Various Chemical Functionalities by an				
			AP-DBD-CVD Process	229			
	8.4	Appli	cations of Adhesion Improvement				
			Atmospheric Pressure Plasma Treatments	240			
		8.4.1	Copper/Epoxy Adhesion in				
			Electronics Industry	240			
		8.4.2	Aluminum to Polyethylene Adhesion for				
			Food Packaging	242			
		8.4.3	Improving Adhesion between Vulcanized				
			and Silicone Rubbers	243			
	8.5	Concl	usion	246			
	Refe	erences		246			
	4 44	•	Y The Continue Contin				
9	1						
			rs Using DBD-based Plasma	251			
			Ambient Pressure	251			
	Michael Thomas, Marko Eichler, Kristina Lachmann, Jochen Borris, Alena Hinze and Claus-Peter Klages						
	9.1						
	9.1		o Functionalization with	252			
	9.2		gen-Containing Gases	253			
			Amino Functionalization Using a DBD	253			
		9.2.1	Amino Functionalization Using an	200			
		9.2.2	AC Corona Discharge	259			
	0.2	Adho	sion Promotion by Amino Functionalization	20)			
	9.3		Nitrogen-Containing Gases	262			
		9.3.1	Adhesion Promotion by Amino	202			
		9.3.1	Functionalization Using DBD	262			
		022	Adhesion Promotion by Amino	202			
		9.3.2	Functionalization Using an AC Corona				
				268			
	0.4	Com	Discharge lusion	270			
	9.4			271			
			dgements	271			
	References						

x Contents

10	Adhesion Improvement of Polypropylene						
	through Aerosol Assisted Plasma Deposition						
	at Atmospheric Pressure						
	Marjorie Dubreuil, Erik Bongaers and Dirk Vangeneugde						
	10.1						
	10.2	2 Experimental					
		10.2.1	Experimental Setup	278			
		10.2.2	Contact Angle (CA) Measurements	281			
		10.2.3		281			
		10.2.4		282			
		10.2.5	Infrared Spectroscopy	283			
		10.2.6	Peel Tests	283			
	10.3	Result	s and Discussion	283			
	10.4	Concli	usions	295			
	Ackr	nowledg	gments	296			
	Refe	rences		296			
11	701	E.C	/ T 1				
11		The Effect of Helium-Air, Helium-Water Vapor,					
	Helium-Oxygen, and Helium-Nitrogen						
	Atmospheric Pressure Plasmas on the						
			rength of Polyethylene	299			
			guez-Santiago, Andres A. Bujanda,				
	Kenneth E. Strawhecker and Daphne D. Pappas 11.1 Introduction						
	11.1			300			
	11.2		mental Approach	301			
			Plasma System and Materials	301			
		11.2.2	Water Contact Angle Measurements	302			
			AFM Images	302			
			XPS Measurements	303			
	44.0		Adhesion Testing	303			
	11.3		s and Discussion	304			
			Water Contact Angles	304			
			XPS Analysis	304			
			AFM Results	308			
			T-Peel Tests	310			
		Conclu	(2)	311			
	Acknowledgements			312			
	References						

12	Atmospheric Plasma Surface Treatment of						
	Styrene-Butadiene Rubber: Study of Adhesion						
	and Ageing Effects						
	Cátia	Cátia A. Carreira, Ricardo M. Silva, Vera V. Pinto,					
	Maria	Maria José Ferreira, Fernando Sousa,					
	Ferna	Fernando Silva and Carlos M. Pereira					
	12.1	Introdu	action	316			
	12.2	Experir	nental	319			
		12.2.1	Characterization	320			
	12.3	Results	and Discussion	320			
		12.3.1	Plasma Treatment	320			
		12.3.2	Ageing Effects	323			
	12.4	Conclu	sions	325			
	Ackn	owledge	ements	325			
	Refer	ences		326			
10	A 4 a	amb ani a	Plasma Treatment in Extrusion Coating				
13	Atmospheric Plasma Treatment in Extrusion Coating: Part 1 Surface Wetting and LDPE Adhesion to Paper						
	Mikko Tuominen, J. Lavonen, H. Teisala,						
	M. Stepien and J. Kuusipalo						
		Introdu	THE CO. 100	330			
		Experir		332			
			and Discussion	336			
	10.0		Performance of Atmospheric	0.0,0			
		10.0.1	Plasma Treatment Unit	336			
		13.3.2	Wetting of Paper Surface	340			
			Adhesion between LDPE Coating and Paper				
	13.4	Conclu		350			
	Ackn	owledge		351			
		ences		351			
		10 10:					
14			Plasma Treatment in Extrusion Coating:				
	Part 2 Surface Modification of LDPE and						
		oated Pa	•	355			
			inen, J. Lavonen, J. Lahti and J. Kuusipalo	25			
	14.1	Introdu		356			
	14.2	Experi	mental	359			

xii Contents

	14.3	Results	s and Discussion	363	
		14.3.1	Performance of Atmospheric		
			Plasma Treatment Unit	363	
		14.3.2	Surface Wetting of LDPE and		
			PP Coated Paper	365	
		14.3.3	Printability of LDPE and PP Coated Papers	370	
		14.3.4	Sealability of LDPE and PP Coated Papers	373	
		14.3.5	Friction, Gloss and Barrier Properties		
			of LDPE and PP Coated Papers	376	
	14.4	Conclu	isions	377	
	Ackn	owledg	ements	379	
	Refer	ences		379	
15	Achie	wing E	nhanced Fracture Toughness of		
13		-			
	Adhesively Bonded Cured Composite Joint Systems Using Atmospheric Pressure Plasma Treatments				
	Amsarani Ramamoorthy, Joseph Mohan, Greg Byrne,				
	Neal Murphy, Alojz Ivankovic and Denis P. Dowling				
		Introdi		384	
				385	
	15.3		eterisation Techniques	387	
			Water Contact Angle Measurements	387	
		15.3.2	1	387	
			Double Cantilever Beam Test	387	
	15.4		s and Discussion	388	
		15.4.1	Surface Activation - Water Contact Angle		
			(WCA) Measurements	388	
		15.4.2	Surface Chemistry - XPS Examination	390	
		15.4.3	Mechanical Testing - Fracture Toughness	392	
	15.5	Conclu	isions	393	
	Acknowledgement			393	
	References			393	