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Dr. Robert H. Lacombe
Chairman
Materials Science and Technology
CONFERENCES, LLC
3 Hammer Drive
Hopewell Junction, NY 12533-6124
Tel. 845-897-1654, 845-592-1963
FAX 212-656-1016
E-mail: rhlacombe@compuserve.com

REMEMBRANCE OF SYMPOSIA PAST: POLYMER SURFACE MODIFICATION 1993

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EDITORIAL COMMENTS

In view of the upcoming tenth in the POLYMER SURFACE MODIFICATION symposium series this issue will have a retrospective look going back to the very first symposium which was sponsored by the IBM Company and held in Las Vegas, Nevada, November 3-5, 1993. The proceedings of this meeting were documented in a hard bound volume edited by MST's director Dr. Kash Mittal and published by VSP in 1996 under the title POLYMER SURFACE MODIFICATION: RELEVANCE TO ADHESION (VSP, Utrecht, The Netherlands, 1996, hereinafter referred to as SMOD1993). As this was nearly 23 years ago the volume has long since been out of print and the publisher VSP has also folded. Indeed many of the contributors have also gone away or have long since retired. However, the topic of polymer surface modification remains as vibrant as it ever was since it has very strong relevance to the everyday uses of polymers, one of the world's most commonly used materials. Thus the topic of this issue's essay will be an overview and remembrance of this seminal volume.

As nearly everyone is aware the polymer materials have a number of highly desirable properties including, good strength, light weight and ease of manufacture using a range of molding, extrusion and coating methods. However, the low surface energy of these materials makes them very difficult to bond to which effectively excludes the untreated materials from uses such as packaging materials and in all manner of composites. Surface modification technologies step in at this point by making the polymer surface amenable to bonding without sacrifice of the desirable bulk properties. Indeed it is no exaggeration to state that without surface modification the polymer materials would be in comparatively limited use today.

Also in this issue are details of the upcoming tenth in the POLYMER SURFACE MODIFICATION symposium series and notification of other important meetings being held worldwide.

POLYMER SURFACE MODIFICATION CIRCA 1993

The SMOD1993 volume comes in 4 parts with the first 2 devoted to the very much in vogue plasma and laser modification methods. Part 3 deals with the much longer established methods such as flame, corona, UV-Ozone, chemical and surface grafting methods. It is interesting to note as pointed out in the paper by Strobel et al (SMOD1993, P.233) that polymer surface modification has a rather long history apparently going back to the 1950's when flame and corona treatment methods were used to improve the wetting and

adhesion properties of polyolefin films. This is rather remarkable since the two most widely available polymers, nylon and polyethylene, really did not enter manufacturing production till about 1940. Thus the early polymer materials had scarcely been available commercially for even 10 years than it was found necessary to modify their surface properties in order to incorporate them into useful products.

Part 1. Plasma Surface Modification Techniques

The first part of SMOD1993 deals with the then relatively novel plasma methods for modifying polymer surfaces. Both low pressure and atmospheric pressure methods are discussed. The low pressure method which is carried out under a moderate vacuum of about 1 Pa was by far the most common plasma technique. The atmospheric plasma method, where the plasma is generated under ambient conditions, was quite new at the time. The atmospheric pressure method, however, has over time become the dominant one for plasma treatment in manufacturing operations since it does away with the cumbersome and expensive vacuum equipment needed for the low pressure approach. Of the 9 papers given in this section only 2 deal with the atmospheric pressure method and the remaining use the low pressure technique.

Typical of the papers in this section is the one by Owen and Smith[1]. The importance of this paper lies in the attention it pays to the array of mechanisms that can destroy the desirable effect of the plasma treatment. In the case of Poly(dimethylsiloxane) PDMS the intent of the treatment is to reduce the hydrophobicity of the polymer in order to make it compatible with other materials. In particular the following post treatment behavior can undo the changes induced by the plasma and bring about hydrophobic recovery:

1. Reorientation of surface hydrophilic groups
2. Migration of treated polymer chains from surface to bulk
3. Migration of untreated polymer from bulk to surface
4. Loss of volatile oxygen rich or other polar entities to atmosphere
5. Changes in surface roughness
6. External contamination from atmosphere

Indeed it can be said that one or more of the above processes can subvert any of the plasma treatment methods and thus the need for vigilance whatever the process.

Other topics covered in this section include:

[1] "Plasma Treatment of Polydimethylsiloxane" , Michael J. Owen and Patrick J. Smith, SMOD1993 P.3

- Use of low an atmospheric plasma to improve adhesion of polyurethane-polypropylene composites

- Treatment of fluoropolymers for improved metal adhesion

- Detailed study of the effect of plasma parameters on the chemical, physical, and morphological states at the metal-polymer interface

- Interfacial chemistry of Al and Cu metallization of of untreated and plasma treated polyethylene and poly(ethyleneterephthalate)

- Barrier properties of plasma modified polypropylene and poly(ethyleneterephthalate)

- Surface biomedical effects of plasma treatment of polyurethane

The above list clearly demonstrates the impressive scope of plasma modification of polymer surfaces and could indeed form the basis of a current day symposium on the topic.

Part 2: Laser Surface Modification Techniques

Laser technology came along well after plasma methods were already in use. Though the founding concepts of stimulated and spontaneous emission of electromagnetic radiation were established already by Einstein in 1917 it was apparently not until 1960 that Theodore Maiman demonstrated the first working laser. Other important researchers carried the work further so that by the time of the symposium a wide variety of laser sources were available covering a wide range of the electromagnetic spectrum.

Bruer et al (SMOD1993, P. 185) point out that the classic surface treatment methods such as plasma, wet chemical and mechanical approaches are handicapped by the fact that they are not applicable to many polymers and are limited in practical use because of the need for special treatment conditions. Buchman et. al.(SMOD1993, P. 119) go on to point out that the classical methods also tend to be destructive, poorly controllable and tend to introduce undesirable changes in the morphology and composition of the surface such as cracks, pitting and contamination.

In any case the use of laser radiation to modify polymer surfaces adds a potent new instrument to the surface modifiers tool box. The applications covered in this section include:

- Polymer surface modification with UV eximer radiation

- Photolytic surface modification with UV laser radiation

- Laser induced adhesion enhancement of polymer composites

- Eximer laser induced photochemical modification and adhesion improvement of fluororesin surfaces

- Photochemical surface modification of poly(propylene) for improved adhesion by eximer laser

Part 3: Other/Miscellaneous Surface Modification Techniques

This section covering the broad range of surface modification methods is consequently to largest with fully 13 papers ranging from gas phase methods to the use of micro-organisms to achieve desired surface properties. As there are far too many papers to cover in the limited space available for this essay we will focus on two of the most innovative and unconventional ones.

First is the unique paper by Silverstein and Sadovsky on “Surface Modification of Drawn Gel-cast Ultraihigh Molecular Weight Polyethylene Films”. (SMOD1993, P. 401)

Ultra-high molecular weight polyethylene (UHMWPE) is very similar in its characteristics to high-density polyethylene (HDPE) but with an impressive list of superior properties Including:

- Resistant to concentrated acids and alkalis, as well as numerous organic solvents

- Highly resistant to corrosive chemicals

- Has extremely low moisture absorption and a very low coefficient of friction

- Is self-lubricating and is highly resistant to abrasion

- Its coefficient of friction is comparable to that of polytetrafluoroethylene (PTFE, Teflon), but has better abrasion resistance.

- Fibers have yield strengths as high as 2.4 GPa and and density as low as 0.97 g/cm^3 giving them a strength-to-weight ratio eight times that of high-strength steels.

The above list of properties clearly make UHMWPE an ideal candidate as a reinforcing agent in high performance light weight composites. Unfortunately the very high crystallinity makes it nearly impossible to bond to any other polymer such as the epoxies. The lower molecular weight polyethylenes can be bonded to other materials but require surface treatment with chromic acid and this harsh acid significantly impacts the properties of UHMWPE. Silverstein

and Sadovsky sidestep this problem by dealing with UHMWPE films instead of fibres and find that plasma and acid treated films can be bonded with epoxy and achieve a cohesive failure strength approaching that of the epoxy.

It is clear the even today the problem of implementing UHMWPE into polymer composites is very much one of the frontier problems in composite technology.

The second paper of interest is the highly unusual and innovative work of Pisanova and Zhandarov entitled "Modification of Polyamide Fiber Surfaces by Micro-organisms" (SMOD1993, P. 417)

This work clearly highlights the fact that the technical community have not overlooked any of the possible methods of polymer surface modification. The authors point out that micro-organisms are well known to degrade the properties of polymer materials. However, they also point out that polymer fibers are highly oriented and close packed so that micro-organism attack can be limited to the fiber surface thus presenting an opportunity for selective surface modification.

The authors go into the pertinent details of selecting the right micro-organisms and the right nutrient conditions to achieve satisfactory results. Though only a small number of composite systems were investigated it is interesting to note that an improvement of up to 80% in interfacial shear strength could be achieved in certain cases. To the best of my knowledge there has been no followup on this kind of work. However, the current interest in GREEN CHEMISTRY may lead to a revival of this intriguing technology.

PART 4: General Papers

This section contains a set of 7 papers dealing mostly with the characterization of treated surfaces. It is one thing to treat a surface by whatever method and quite another to know exactly what you have done. The paper by Grundke et al entitled "Physico-chemical Properties of Surface-modified Polymers" (SMOD1993, P. 431) gives an overview of several methods for investigating the physico-chemical state of a treated surface including:

- Inverse gas chromatography for investigating nature of surface interactions
- Wetting measurements such as contact angle to evaluate the surface free energy state
- electrokinteic methods such as zeta potential to evaluate nature of prevalent surface forces such as van der Waals, acid/base, and coulomb interactions

- X-ray Photoelectron Spectroscopy (XPS) to evaluate surface chemical composition and nature of chemical bonding

A number of specific examples are examined in detail to give a feel for how the above methods can be applied and what information can be obtained.

Another plasma surface modification method is presented by Heilman et al in a paper entitled “Laser Annealing and Surface Modification of Plasma Polymer-metal Composite Films” (SMOD1993, P. 525). This paper introduces the twin process to standard plasma surface modification which is plasma surface polymerization. In the standard plasma treatment reactive ions in the plasma gas act on the polymer surface by introducing reactive species to the surface, removing low molecular weight debris, initiating cross linking and also causing chain scission. At the end of the process the plasma gasses disappear and a chemically modified and activated surface is left behind. With the plasma polymerization approach, the reactive plasma also contains free radical species which can deposit on the surface and then polymerize in situ leaving behind an entirely new surface film after the plasma field is removed. The plasma polymerized films tend to show very good adhesion and form continuous layers of very low thickness. One of the key properties of these coatings is that depending on conditions a number of free radical and functional groups can be left behind which can serve as an effective adhesion layer for further overcoats. The authors go on to use the plasma polymerization method combined with laser annealing to incorporate metal particles onto polymer surfaces to modify the optical properties. The metal particles are trapped on the surface by the plasma film and laser annealing causes the particles to coalesce within the film.

All in all the first in the polymer surface modification series gave a very robust start to a succession of 8 further meetings where the topic has not only shown sustained interest but also continues to surprise with ever more ingenious applications.

CALENDAR OF EVENTS

The 11th International Conference on Polyimides & High-Performance Polymers

This symposium also known as STEPI11 will be held in Montpellier, France, during June 2-5, 2019

Deadlines

Registration Opening : January 1, 2019

Early Bird Registration : April 10, 2019

Abstract Submission :
December 2018 to May 10, 2019

For further details Please visit:

http://stepi.umontpellier.fr
or
http://STEPI11

This will likely be the only international meeting on high performance polymers in 2019. MST presented its last symposium on polyimides at the Florida Institute of Technology, Melbourne, Florida, November 9-11, 2009. Apparent waning interest in this topic has forced us to discontinue this symposium series. It is thus heartening to hear that the topic still garners interest at least in Europe.

Tenth International Symposium on Polymer Surface Modification Relevance to Adhesion

To be held June 19-21, 2019 in collaboration with the Rochester Institute of Technology, Rochester, New York, USA

Symposium History and Motiviation

This the 10th symposium in the series which continues the tradition set by the first in the series entitled: "Polymer Surface Modification: Relevance to Adhesion" which was held in Las Vegas, NV, 1993. As with its predecessors, this symposium will be concerned with the technological areas where surface modification is a key technology which allows for the processing and manufacture of products which would otherwise be unobtainable.

Proper adhesion characteristics are vital to the success of any practical implementation of polymer materials. Though polymers are generally not very adhesionable, careful surface modification can result in greatly improved adhesion without altering bulk properties.

Audience and Participation

This symposium is organized to bring together scientists, technologists and engineers interested in all aspects of polymer surface modification, to review and assess the current state of knowledge, to provide a forum for exchange and cross-fertilization of ideas, and to define problem areas which need intensified efforts.

SUBMITTING A PAPER

This symposium is being organized by MST Conferences under the direction of Dr. K. L. Mittal, Editor, Reviews of Adhesion and Adhesives. Please notify the conference Chairman of your intentions to present a paper as early as possible. An abstract of about 200 words should be sent by March 4, 2019 to the conference chairman by any of the following methods:

E-mail: rhl@mstconf.com
FAX: 212-656-1016
Regular mail:

Dr. Robert H. Lacombe
Conference Chairman
3 Hammer Drive
Hopewell Junction, NY 12533

Contact by phone: 845-897-1654; 845-592-1963
Full conference details and registration via the Internet will be maintained on our web site:

http://mstconf.com/surfmod10.htm

Click below to get on the symposium mail list:

www.mstconf.com/resp-spring-2019.htm

AMONG TOPICS TO BE COVERED ARE:

Surface Modification Techniques

- Plasma, ultraviolet, corona, laser, ion beam, atmospheric plasma, flame ...
- Mechanical roughening
- Monolayer deposition, grafting and wet chemical

Polymer Surface Modification for Adhesion Improvement Of:

- Metal layers (metallized plastics)
- Organic coatings, inks, composites, adhesive joints, microorganisms

Applications and Surface Characterization

- Packaging, composites
- Biomedical applications
  i. implants
  ii. sterilization
  iii. improved cell adhesion
- Microelectronics, aerospace, marine...
- All methods for characterization of surface chemistry and morphology, (Contact Angle, XPS, SIMS, AFM ...)

0RGANIZERS AND CONTACT INFORMATION

Dr. Gerald Takacs
Department of Chemistry
RIT
85 Lomb Memorial Drive
Rochester, NY 14623
Tel. (585) 475-2047
FAX: (585) 475-7800
E-mail: Gatsch@rit.edu

Dr. K .L. Mittal, Director
Heritage Executive Suites
2537 Route 52, Suite 1
P.O. Box 1280
Hopewell Junction, NY 12533-1280
Tel. 845-897-1654
FAX: 845-897-2361
E-mail: klm@mstconf.com

Dr. R. H. Lacombe
Conference Chairman
3 Hammer Drive
Hopewell Junction, NY 12533
USA
Tel. 845-592-1963
FAX: 212-656-1016
E-mail:rhl@mstconf.com

3- Day Impact Course: The Chemistry, Physics & Mechanics of Surface Science and Adhesion

May 8-10, 2019
Courtyard by Marriott, Stewart-Newburgh, New York

Topics to be Covered

I. Surface Contamination and Cleaning
II. Theories or Mechanisms of Adhesion
III. Contact Angle, Wettability and Adhesion
IV. Investigation of Interfacial Interactions
V. Surface Modification Techniques including Plasma
VI. Ways to improve Adhesion of Organic Coatings
VII. Silanes and Other Adhesion Promoters
VIII. Adhesion Aspects of Thin Films
IX. Adhesion Measurement of Films and Coatings
X. Basics of Adhesion Measurement
XI. Residual Stress and Material Mechanical Properties
XII. Setting Adhesion Requirements for Coating Applications
XIII. Adhesion Measurement at Atomic and Molecular Level
XIV. Fundamental Adhesion Applications

Audience: Scientists and professional staff in R&D, manufacturing, processing, quality control/reliability involved with adhesion aspects of coatings and adhesion sensitive applications.

Level: Beginner- Intermediate; introduction/overview

Prerequisites: Elementary background In chemistry, physics or materials science.

Duration: 3 days

Course fee and materials: $1,295, includes break refreshments, complete set of lecture notes and copy of handbook and reference guide ADHESION MEASUREMENT METHODS: THEORY AND PRACTICE, (CRC PRESS, 2006)

For detailed information and registration:

www.mstconf.com/AdhesionCourse.htm

Contact Information

Dr. K. L. Mittal & Dr. R. H. Lacombe
Tel. 845-897-1654 & 845-592-1963
E-mail: rhl@mstconf.com