MATERIALS SCIENCE AND TECHNOLOGY NEWSLETTER

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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

EDITORIAL COMMENTS

POLYMER SURFACE MODIFICATION: MORE SUBTLE AND UBIQUITOUS THAN YOU THINK

In this issue of the Newsletter we shift focus to the subject of polymer surface modification. This topic is highly apropos in view of the upcoming Tenth International Symposium on Polymer Surface Modification: Relevance to Adhesion, to be held at the Rochester Institute of Technology, Rochester, New York, USA, June 19-21, 2019. In what follows we leave the beaten path somewhat and discuss applications related to food processing and surface treatment to minimize rather than promote adhesion.

All readers are cordially invited to join the symposium either to present a paper on their current work in this field or to simply attend and greatly expand their awareness of current developments. Further details are available on the conference web site at:

www.mstconf.com/surfmod10.htm

POLYMER SURFACE MODIFICATION

Mainstream Applications

In a resent volume Rory Wolf[1] gives a fairly exhaustive overview of many of the most common polymer surface modification methods with an emphasis on plasma treatment and the newly developed atmospheric plasma processing. The number of coating technologies covered is quite amazing. The volume covers some 12 different manufacturing scale coating methods including:

1. Gap coatings
2. Immersion coatings
3. Curtain coatings
4. Rotary screen coatings
5. Gravure coatings
6. Reverse roll coatings
7. Metering rod coatings
8. Slot die (extrusion) coatings
9. Hot melt coatings
10. Flexographic coatings
11. Silk screen coatings
12. Nano coatings

All of the above are large scale manufacturing applications where surface modification is being used to improve wetting and thus also adhesion giving rise to a more durable coating. All of these topics are of potential interest to the above mentioned symposium. However, in what follows we explore less well known applications.

Better Berries Through Plasma Cleaning

It seems that scarcely a year goes by but we read news headlines covering an outbreak of food poisoning traced to a well known restaurant chain and typically caused by either E-coli or salmonella bacteria. Fruits and vegetables seem to rank high on the list of known vectors for transmitting these pathogens through the food chain to the unsuspecting restaurant goer. The skins of all fruits and vegetables are of course biopolymers and interestingly surface modification through atmospheric plasma has been shown to be an effective deterrent to bacterial contamination. A good example has been demonstrated by research team under the direction of Dr. Brendan Niemira[2], a microbiologist at the U.S. Department of Agriculture's Eastern

[1] "Plastic Surface Modification: Surface Treatment and Adhesion", by Rory Wolf (Carl Hanser Verlag, Munich 2010)

[2] "Cold Plasma Proving to Be Hottest New Food Safety Treatment" Food Safety News, December 7, (2016)

Regional Research Center in Wyndmoor, PA. The USDA team of scientists demonstrated that cold plasma (CP, another name for Atmospheric Plasma) can kill pathogens such as Salmonella and E. coli on blueberries.

The Food Safety News writeup makes a highly cogent case for the use of Atmospheric Plasma in treating blueberries including the following:

- Blueberries have become increasingly popular diet items due to their antioxidant and other nutritional benefits.

- However, they are typically eaten raw and are susceptible to contamination by a number of pathogens such as the human norovirus which is a common agent in foodborne illness.

- In addition blueberries are prime prospects for improved decontamination procedures due to their fragile nature and short shelf life which puts a lot of pressure on the need to move them through harvest and packaging.

- Current preventative procedures rely on chemical washes and stepped up hygienic food handling procedures many of which have yet to be effectively applied to fresh cut produce.

- The USDA researchers demonstrated that the cold plasma removed more than 99.9% of the two viruses being studied in under two minutes or less.

- The cold plasma treatment was also shown to inactivate spoilage microorganisms on blueberries without effecting firmness, color or anthrocyanin concentration. In addition the cold plasma technology is environmentally friendly and sustainable without the need for onsite storage of chemicals or large volumes of water for post-treatment rinsing.

Figure 1 Photo of Atmospheric Plasma flame treating a sample of blueberries. (From ref. 2)

Going by this account it is clear that food processing is on its way to becoming one of the major applications of biopolymer surface modification. Interestingly, however, applications to food processing seem to be just the tip of the iceberg in terms of novel applications of the atmospheric plasma method. A relatively new company, Intrface Technologies[3], seems to have entered the field in a big way by offering the following impressive list of applications:

- Catheter Bonding and activation for coating: Pebax, Nylons, PEEK, Polyimide, Silicone, Carbothane, Estane, HDPE, LDPE, Pellethane, PET, PFA, PVC, Hytrel

- Guidewire Cleaning and oxidation for coating: Stainless Steel and Nitinol

- PCR plate sterilization, activation and functionalization: Polypropylene (PP), Polycarbonates (PC)

[3] Contact at: info@intrfacetech.com

- Glass and Transparent conducting oxide (TCO) thin films for solar and touch screen display industries

- Semiconductor and Electronics encapsulation for high reliability environments in Automotive, Solar, Space and Defense applications

- Oil & Gas and plumbing: High performance tubing and pipe assemblies. Marking and identification of low surface energy external substrates including Nylons, PEEK, rubber, HDPE, LDPE

- Composites for aerospace, UAV / drone, high performance vehicles and other lightweighting applications: epoxies, BMI, thermoplastic hybrid polypropylene (PP)

- MEMS and Microfluidics manufacturing and assembly including Polydimethylsiloxane (PDMS) functionalization and glass cleaning

- Carbon nano tube (CNT) and Graphene cleaning and activation

Thus it seems that the number of applications of polymer surface modification is apparently endless and we hope to explore as many as possible at the tenth in the POLYMER SURFACE MODIFICATION symposium series.

Surface Modification to Reduce Adhesion

All of the instances listed under Mainstream Applications above are cases where surface modification is employed to promote adhesion. When applying coatings, for example, one invariably wants good adhesion in order to promote coating durability. However, more recently there has been a trend toward creating surfaces with poor adhesion properties. Examples include self cleaning window glass for low maintenance enclosures and self cleaning fibers for stain resistant clothing. One of the earliest efforts in this direction was carried out by Prof. Thomas McCarthy and his students[4] at the University of Massachusetts.

These researchers started with a moderately hydrophobic coating of poly(propylene), herinafter designated PP, which has advancing and receding contact angles of 105 and 88 degrees respectively. Then the PP is etched with argon plasma along with a sample of poly(tetrafluoroethylene), hereinafter PTFE. The argon plasma simultaneously sputters the PTFE creating a reactive fluorocarbon plasma while at the same time etching the PP. As the PP coating is etched it is also fluorinated as was determined by ESCA analysis. Figure(2) shows AFM micrographs of the untreated PP and after plasma treatment for up to 120 minutes. What is clear from the figure is that as the PP surface becomes more variegated The contact angle increases accordingly giving rise to an ultrahydrophobic surface. This is in accordance with the theories of Wenzel and Cassie and Baxter which predict that the cosine of the contact angle should scale as the surface roughness factor which is defined as the geometric area divided by the actual area which is always greater for a rough surface.

Thus we begin to get a glimpse of the enormous range of applications of polymer

[4] "Ultrahydrophobic Polymeric Surfaces Prepared Using Plasma Chemistry", Meng. C. Hsieh, Jeffrey P. Youngblood, Wei Chen and Thomas McCarthy, in Polymer Surface Modification, Relevance to Adhesion, Vol. 2, pp. 77-89 (Ed. K. L. Mittal, VSP Utrecht, 2000)

surface modification from treating agricultural products to creating self cleaning surfaces. It will be interesting to see what new applications emerge in the upcoming 10th in the Polymer Surface Modification, Relevance to Adhesion symposium series discussed below.

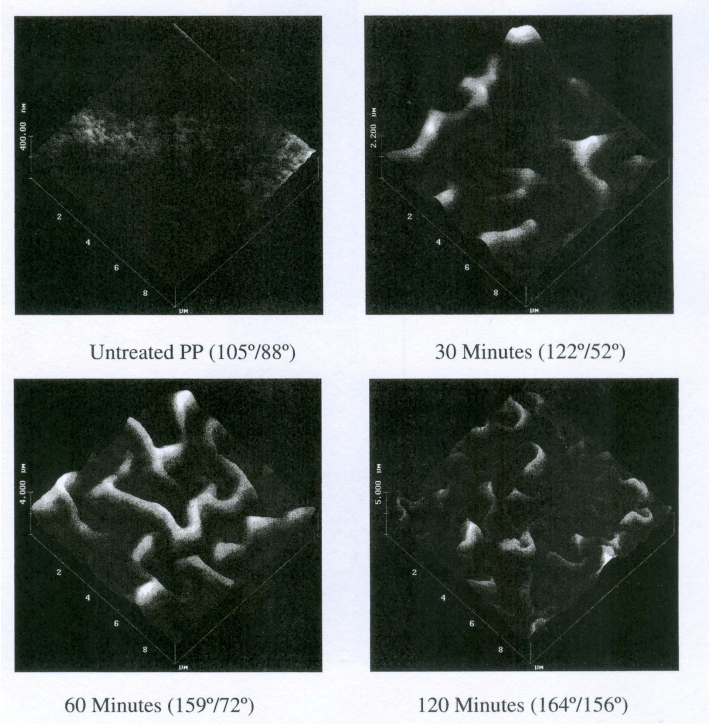


Figure 2 AFM micrographs showing the increase in roughness of a poly(propylene) surface with increased exposure to an argon ion plasma. The numbers in parentheses are the advancing and receding contact angles of the respective surfaces. (Adapted from figure 9 of ref. 3)

CALL FOR PAPERS
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

RIT

SYMPOSIUM HISTORY AND MOTIVIATION

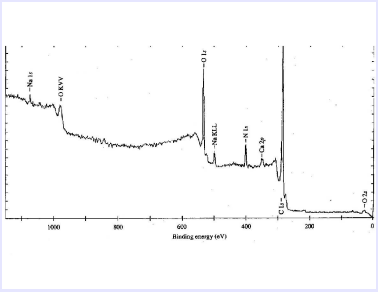
This the 10th symposium in the series which continues the tradition set by the first in the series entitled: "Polymer Surface Modification: Relevance to Adhesion" which was held in Las Vegas, NV, 1993. As with its predecessors, this symposium will be concerned with the technological areas where surface 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.

Photo courtesy of Plasmatreat

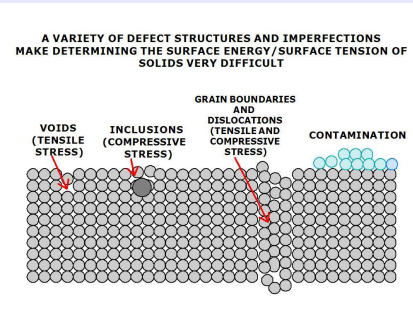
AUDIENCE AND PARTICIPATION

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:

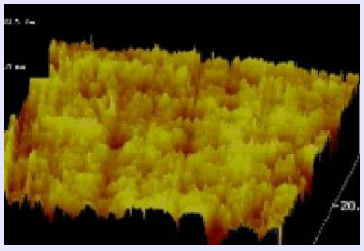
Dr. Robert H. Lacombe
Conference Chairman
3 Hammer Drive
Hopewell Junction, NY 12533, USA

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:

ONLINE RESPONSE FORM: www.mstconf.com/resp-spring-2019.htm



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

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 ...)