

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, 845-227-7026
FAX 212-656-1016
E-mail: rhlacombe@compuserve.com

FOCUSING ON SURFACE MODIFICATION TECHNOLOGIES

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EDITORIAL COMMENTS

It is our pleasure in this issue of the Newsletter to announce the preliminary programs for what promise to be two most interesting and informative symposia scheduled for the week of June 11, 2007 in Cincinnati Ohio. In particular, readers should take note of the following two symposia:

SIXTH INTERNATIONAL SYMPOSIUM ON POLYMER SURFACE MODIFICATION: RELEVANCE TO ADHESION; to be held in Cincinnati, Ohio, June 11-13, 2007.

SIXTH INTERNATIONAL SYMPOSIUM ON SILANES AND OTHER COUPLING AGENTS; to be held in Cincinnati, Ohio, June 13-15, 2007.

The preliminary programs for these two symposia are listed at the end of this newsletter along with detailed information on registration and hotel accommodations. The staff of MST CONFERENCES and the faculty of the Chemical Engineering Department of the University of Cincinnati cordially invite all readers of this letter to participate in these events.

In keeping with the themes of the above symposia the essays in this issue will look into two interesting and important aspects of surface modification technology. The first topic deals with the ever growing field of plasma treatment at atmospheric pressure. I remember the early days of plasma treatment where everything had to be done in a bulky and not too convenient vacuum systems. The constraints imposed by having to work in a closed vacuum system ruled out the use of plasma modification in a number of applications that could have greatly benefitted from this technology. Atmospheric plasma treatment has now removed a number of these constraints and plasma treatment can now be used in large scale applications that were previously beyond reach. A number of papers dealing with this topic will be presented at the June symposium and interested readers are most cordially invited to join us in Cincinnati at that time to learn about the latest developments and discuss technical matters in general with a number of the world's leading experts in this area.

The second topic deals with the durability of silane treated interfaces. In particular, silane treated glass fibers in polyester/fiberglass composites used in the boating industry have shown remarkable durability and we will try to uncover some of the fundamental reasons behind this most remarkable stability.

ATMOSPHERIC PRESSURE PLASMA TREATMENT

Ever wonder how they get the ink to stick to all those plastic packages and plastic bottles that you find on nearly every shelf in the supermarkets? If you take any common ink pen and try to write on these surfaces you quickly find that if you can make any kind of mark at all, whatever mark you do make is very easily smudged by swiping over it with a light touch of the finger. The basic problem comes down to the fact that most inks that readily mark common paper simply do not wet the plastic surfaces which are used in the preponderant number of packaging applications. One way around this problem is to use inks based on strong organic solvents that actually penetrate and swell the polymer material being used. This approach, however, has the decided disadvantage that the volatile organic solvents (alias VOC's) that must be used are almost inevitably considered to be environmentally unfriendly and in consequence get heavy scrutiny from the various environmental agencies. This becomes a rather major problem when one considers the enormous volume of polymer based packaging materials that are distributed throughout the world every year.

Another approach is to use some sort of polymer surface modification technology which can make the very outer surface of the plastic chemically receptive to the ink one wants to apply while leaving the overwhelming bulk of the material unchanged. There are a number of ways of approaching this problem as a quick look at the POLYMER SURFACE MODIFICATION program listed at the end of this letter will quickly confirm. Each approach has its own particular advantages and disadvantages, but for current purposes we will focus on the relatively new approach of plasma treatment under atmospheric conditions.

Large Scale Plasma Treatment of Polypropylene

Next to Teflon and polyethylene, polypropylene is quite like one of the least moisture wettable polymers known to man. However, polypropylene and its derivatives are a favorite packaging material and one would like to be able to print on it with a water based ink. This is clearly a polymer surface modification application and, as an example, the Enercon[®] company (www.enerconind.com) has developed a successful implementation of this technology.

Figure 1 is a photograph of an industrial strength

atmospheric treatment tool for modifying polymer sheet materials. As an example of the capabilities of this type of tool there was a customer need to treat 0.40 mil thickness polypropylene sheet to improve aqueous-based ink adhesion. This application was implemented on a glow discharge plasma system at atmospheric conditions similar to the one shown in the figure. Such a machine can treat sheets from 27-60 in. wide which puts this application well beyond the capabilities of conventional vacuum chamber systems. The improvement in the surface tension of the sheets was determined by surface tension test fluid markers using the ASTM D-2578 standard wettability evaluation method. The surface energy of the sheets was enhanced substantially after atmospheric plasma treatment. However, the real test of performance was how well the sheets took water based ink deposited by a flexographic¹ printer. The sheet was printed from a roll at 200 fpm. The ink was dried in-line with forced air at a temperature of 140 deg F. Untreated, corona treated, and atmospheric plasma treated specimens were then subjected to a tape peel test to determine the adhesion of the ink. A test was performed for each sample with a ½ in. × 2 in. tape² using fresh transparent (clear) pressure-sensitive tape. The tape was applied to the printed side of the film and allowed to remain for 60 sec. During the peel test, the untreated samples exhibited total ink adhesion failure, with all image ink removed with the tape. The corona treated specimens retained approximately 90% of the image ink at its surface. The plasma treated samples displayed 100% ink adhesion, with no residue being removed from the surface. The results unmistakably confirm the effectiveness of atmospheric plasma treatment in enhancing the adhesion of water based inks to polypropylene. It is also clear that this type of treatment need not

¹ The FLEXOGRAPHIC printer is essentially a digital approach to mass printing applications. If you look closely at the pictures in magazines and other mass printed media with a 20 power lens you see an array of colored dots as opposed to a continuous coating.

² The tape test for ink adhesion has been a standard in the printing industry for many years. The advantages and disadvantages of this method are covered in the MST CONFERENCES Short Course on Adhesion Measurement Methods: Theory and Practice which will be given at the June 2007 conference. See registration sheet at the end of the newsletter for details.

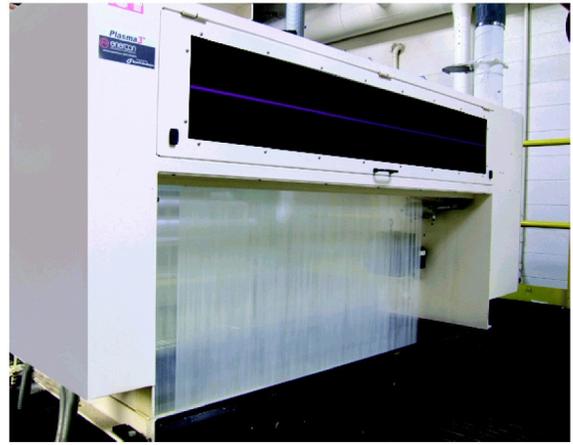


Figure 1 Atmospheric plasma surface modification tool for treating polymer sheet material on an industrial scale. Courtesy Enercon®

be confined to polypropylene sheet materials. In addition, other textile materials which can be successfully treated with this method include polypropylene fibers, polyethylene sheets, poly(ethylene-terephthalate) fiber, Tyvek, nylon, wool, and textile yarns. Further developments and advances in this technology will be discussed in the paper "Advances in Adhesion with CO₂-Based Atmospheric Plasma Surface Modification" by Rory Wolf which is listed in the Plasma Treatment Session of the attached preliminary program.

ENVIRONMENTAL DURABILITY OF SILANE TREATED INTERFACES

In the Summer-Fall 2006 issue of the Newsletter (www.mstconf.com/Vol3No3-2006.pdf) the question of the durability of silane treated interfaces was discussed in relation to the pioneering work of Dr. Edwin Plueddemann then at the Dow-Corning Corporation. Ed used to claim that his goal was to eliminate moisture induced failure in any application for a lifetime durability of 1000 years. In support of this claim he pointed out the remarkable durability of fiberglass reinforced polyester composites used in the hulls of boats. He pointed out that many of these craft had been in the water for 20 years without showing any signs of degradation of bonding between the polyester and the glass fibers. I recently perused an article by Eric Green in a recent issue of Composites Manufacturing³

³ "Built to Last: the Lifetime of Fiberglass Boats", Eric Greene (Composites Manufacturing,

magazine dealing with this very issue. In this most engaging commentary we find that those boats that Ed Plueddemann was praising some 15 odd years ago are still apparently going strong for a total durability of 35 years plus. Notwithstanding Ed's 1000 year benchmark, the fact that these fiberglass composite hulls are still in top notch condition after 35 years in various marine environments is nothing short of extraordinary. Just think of how many other items you can lay hands on that have seen 35 years plus of day to day service and are still not just in working condition but have shown little or no sign of environmental degradation? I happen to have a 100 pound forged steel anvil in my garage that is still quite serviceable after 35 years but has shown considerable signs of surface corrosion and it has not spent a single day in the out of doors much less in a highly corrosive marine environment. A couple of examples abstracted from Mr. Green's article will serve to further illustrate the point:

US Coast Guard Patrol Boat

The US Coast guard decided in the early 1950's to use fiberglass composite materials in their patrol boats which are used for law enforcement and search and rescue missions. These boats are some 40 feet long and sport twin 250 horsepower diesel engines giving them a top speed of 22 knots. In 1972 Owens Corning and the Coast Guard decided to test the condition of the fiberglass panels in one of these boats that was being retired after 20 years of service. It should be noted that environmentally speaking these were not easy going years. Active duty included many years in a highly polluted channel containing considerable quantities of sulfuric acid among other active ingredients. In addition the boat was subjected to fairly extreme temperatures during firefighting activity.

Table 1: Change in mechanical properties of fiberglass section of Coast Guard Patrol boat after 20 years in marine environment. (Data abstracted from Ref. 3)

Mechanical Property	Percentage Change After 20 Years Service

October 2006, page 28) Composites Manufacturing is an official publication of the American Composites Manufacturers Association)

Tensile Strength	(+)3
Compressive Strength	(+)0.08
Flexural Strength	(+)13
Shear Strength	(-)6

Visual inspection of sliced out sections of hull material indicated that neither water nor chemical reactants had entered the laminate. The mechanical properties of tested sections are summarized in Table 1. Curiously enough all but one of the mechanical properties tested actually increased over the 20 year period of service. This might be due to some small amount of crosslinking of the polymer but regardless of what physico-chemical changes occurred the total effect was quite small given the time duration and severity of conditions.

Submarine Hydrodynamic Cowling

Another example of long term service under challenging conditions is supplied by the US Navy. Submarines apparently have a protective shield that surrounds top mast items such as antennas, radar dishes, ... etc. Commonly referred to as a fairwater, this shield not only protects a number of protruding devices but also reduces the hydrodynamic drag on the boat. Originally made out of aluminum, the Navy decided to shift to fiberglass composite materials for improved durability in service. In this application the fiberglass composite not only has to endure all the rigors of salt water and sun on the open ocean but also intense hydrodynamic pressure when the ship is submersed. The fairwater of the USS Halfbeak was tested after 11 years of service in a manner similar to the Coast Guard boat mentioned above. the results are summarized in Table 2.

Table 2: Change in Mechanical properties of fiberglass fairwater from US Submarine Halfbeak after 11 years service. (Data abstracted from Ref. 3)

Mechanical Property	Percentage Change After 11 Years Service
Flexural Strength	(-) 0.95
Flexural modulus	(-) 0.79
Compressive Strength	(-) 2.7
Specific gravity	0

Scanning the data in Table 2 essentially supports the data presented for the Coast Guard boat shown in Table 1. It is quite likely that the changes recorded fall within the limit of error of the physical measurements indicating that the fiber glass composites maintain close to 100% of their physical properties over indefinite time periods under practically the worst environmental conditions one can think of.

Curiously enough the remarkable durability of these materials has had a down side of sorts for the boat manufacturing industry. An article in *Boat/US Magazine*⁴ commenting on data released by the National Marine Manufacturers Association complained that there was a 9% drop in new boat sales from 1997 to 2004 due to the fact that many first time owners were buying used fiberglass boats as opposed to new ones. This apparently due to the excellent quality and lower price of the former as compared to the later. All of which just goes to show that sometimes you just cannot win for losing.

Reliability Without Hermeticity: Relevance to Composites, Microcircuits and Biotechnology

The case of silane treated polyester/fiberglass composites is an example of structures that have achieved reliability with being hermetically sealed from the ambient environment. In particular it is completely certain that moisture and other contaminants are diffusing into the polyester/fiberglass composites where they accumulate to some concentration or another. However, in the case of the fiberglass laminates the moisture and other contaminants seem to simply sit around and do nothing to either chemically or physically degrade the structure. Why this happens is a matter of the thermodynamic equilibrium that prevails as will be discussed below.

This type of problem is of great interest in many industries other than boat manufacturing. The biomedical implant business, for example, would not have the slightest complaint if their devices exhibited indefinite durability under conditions prevailing in vivo. The patients who require implants of some type be it a heart valve or a hip replacement certainly want the implanted device to function reliably as long as possible. As another example, the microelectronics industry is very much concerned for the safety of the intricate fine wiring structures that make up many of the

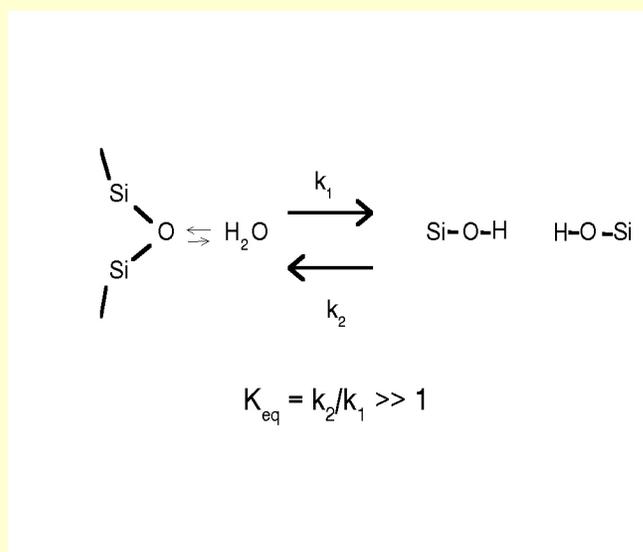


Figure 2 Thermodynamic stability of Oxane bond.

electronic devices which we take for granted these days. As a veteran of the computer industry I can testify that even parts per billion of sulfur in the environment can lay waste to improperly protected micro circuitry. In fact, a large segment of the mainframe industry resorted to hermetic packaging in the late 1970's onward to protect the delicate wiring of these machines. The IBM Company, for instance, enclosed its mainframe chips under a positive pressure of helium contained between a brazed metal cap and a ceramic substrate. Talk about not taking any chances. This approach to reliability works fine for mainframe computers that go for tens of thousands of dollars but the economics simply does not work out for something like a cell phone which also relies on delicate wiring but sells for a couple hundred dollars at most. For these devices one has to achieve reliability without hermeticity as in the case of the fiberglass/polyester composites.

So the question naturally arises as to how the fiberglass/polyester composites manage to survive. Dr. Plueddemann essentially gave the answer in the last paper he ever wrote which was published in a Festschrift⁵ in his honor. The basic answer of course was the use of silane coupling agents between the glass and the polyester resin. But exactly what was the role played by the silane material? This was a particularly pressing question in view of the fact that it was well known that the

⁵ "Reminiscing on Silane coupling Agents", Edwin P. Plueddemann in , *Silanes and Other Coupling Agents: Festschrift in Honor of the 75th Birthday of Dr. Edwin P. Plueddemann*, Ed. K. L. Mittal (VSP, Utrecht, The Netherlands, 1992).

⁴ January 2006 issue.

oxane bonds between silanes and glass or metal oxides are rather easily hydrolyzed which certainly cannot bode well for survival in a marine environment. However, Ed also pointed out that opposing this mechanism is the fact that at equilibrium the oxane bonds have a much greater tendency to reform. Figure 2 presents a highly schematic diagram of what is occurring. Essentially what goes on at the molecular level is a rapid breaking and reformation of chemical bonds. What Dr. Plueddemann pointed out is that the rate constant for Si-O-Si formation is some 1000 times larger than the reverse reaction. At the macroscopic scale this fact translates into what appears to be a nearly indestructible bond despite the known hydrolytic sensitivity of the oxane bond. The simplest thermodynamic description for what is occurring in the reaction depicted in Fig.(2) follows from the well known law of mass action⁶ which in this case can be written as follows:

$$K_{eq}(T) = \frac{[Si-OH]^2}{[Si-O-Si][H_2O]} \quad (1)$$

The symbols in brackets represent the concentrations of the enclosed species. Assume for the moment that the effect of the silane material is to reduce the local moisture concentration. Given this assumption, then by Eq.(1) the equilibrium constant will be increased which will shift the reaction in favor of the stability of the oxane bond. Thus the main action of the silane would be to reduce the local solubility of moisture. Without moisture most other reactants become inactive thereby explaining the bond stability. Most likely more than this is going on since the equilibrium constant will in general depend on the details of the full chemical potential function which governs all chemical equilibria for this type of problem. At a minimum though this analysis suggests that the answer to this type of problem would be greatly aided by a more detailed statistical thermodynamic model of the relevant chemical reactions.

A further example which supports the above analysis came my way quite by accident while investigating the adhesion of polyimide coatings to silicon wafers. For the uninitiated, it should be noted that the top surface of your run of the mill silicon wafer is not pure silicon but silicon dioxide glass since elemental silicon oxidizes rather rapidly. It is not uncommon for the top 1000 angstroms of the wafer to be SiO₂. Thus in this

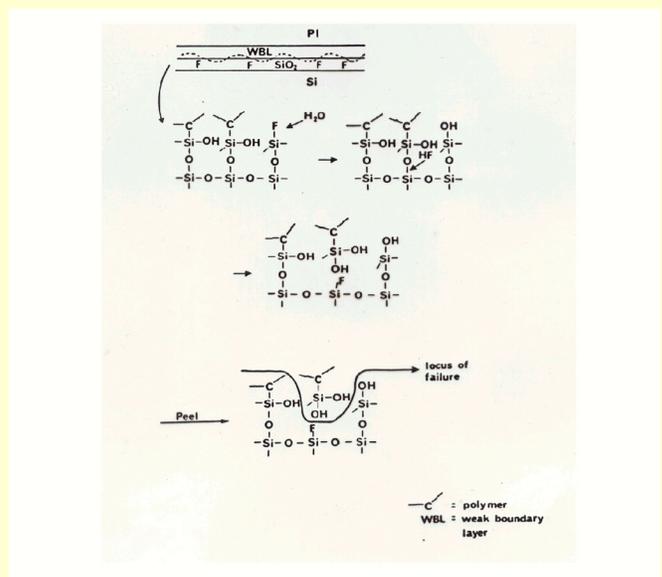


Figure 3 Mechanism of moisture attack at polyimide/glass interface in the presence of trace amounts of fluorine.

experiment I was really looking at the adhesion of polyimide to silica glass. It also turned out by a quirk of fate that the surface also contained a small concentration of about one atomic percent of fluorine which was deposited by a contaminated plasma cleaning unit. The presence of the fluorine caused the adhesion of the polyimide to be extremely sensitive to the ambient humidity conditions. In particular the peel force could decrease by as much as a factor of 20 in going from dry to humid conditions. After much head scratching my colleagues and I finally devised a mechanism for what was going on as shown in Fig.(3). The diagram shows a water molecule first abstracting a fluorine atom from a silicon atom thereby forming hydrofluoric acid (HF) and leaving behind a hydroxyl group. The HF then proceeds to attack the C-O-Si bonds which are providing the main coupling of the polyimide to the silica surface thus greatly reducing the apparent adhesion. What is of interest, however, is the first step where the water molecule first abstracts the fluorine thereby creating HF. This is clearly a reversible reaction similar to that shown in Fig.(2) and gives rise to the same consequences, namely that the equilibrium can be dramatically shifted by the local moisture concentration. The same can also be said of the reaction which leads to the cleavage of the C-O-Si bonds which by way of chain reaction are sensitive to the local HF concentration which depends in turn on the local moisture level. All reactions are completely reversible which implies a restoration of adhesion upon removal of the moisture which is precisely what we observed. Finally, introducing a silane adhesion promoter at the interface greatly reduced this effect implying that the silane is acting in the

⁶ See for example "Thermodynamics", H. B. Callen (John Wiley & Sons, 1960) p. 207 or nearly any physical chemistry text.

same manner as it does for the polyester/fiberglass system. In both cases the silane is shifting the chemical equilibrium toward stable bonds by lowering the local moisture solubility.

SYMPOSIA ON POLYMER SURFACE MODIFICATION AND SILANE ADHESION PROMOTERS

In the above brief essays we have touched upon some of the applications and nuances of surface science as exemplified by plasma modification and silane adhesion promoters. Needless to say there is much more to these topics than can possibly be covered in such limited space. This makes it desirable to bring those who deal with these matters in greater detail together to discuss the latest developments and findings. The reader who wishes to stay abreast of current technologies and applications in these areas will find the following symposia to be very fruitful, efficient and satisfying venues to learn the latest progress in these areas and also an excellent opportunity to network among many of the leading practitioners from all over the globe.

PRELIMINARY PROGRAM SIXTH INTERNATIONAL SYMPOSIUM ON POLYMER SURFACE MODIFICATION: RELEVANCE TO ADHESION; To be held June,11-13, 2007; University of Cincinnati, Cincinnati, Ohio, USA

This symposium 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. It is also our distinct privilege to be able to hold the sixth symposium in the series in collaboration with Prof. Wim van Ooij and his group at the University of Cincinnati. Prof. van Ooij has been an active researcher in the field and he and his group look forward to hosting this symposium and greeting all participants from both academia and industry from all corners of the globe. 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. 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.

The invited speakers have been selected so as to represent widely differing disciplines and interests, and they hail from academic, governmental and industrial research laboratories. This meeting is planned to be a truly international event both in geographic coverage as well as in spirit. Please **NOTE** that the address given may apply only to the highlighted speaker.

RADIATION AND FLAME TREATMENT

R. Bongiovanni and A. Priola; Department of Materials Science and Chemical Engineering Politecnico di Torino ITALY; **Adhesion of Fluorinated UV-cured Coatings on Functionalised Polyethylene**

M. Masudul Hassan, M. Rabiul Islam and Mubarak A. Khan; Technical University of Berlin, Polymertechnik/Polymerphysik, Fasanenstr. 90, D-0623 Berlin, GERMANY; **Effect of Radiation on Surface Modification of Cellulose with Acrylamide**

Takaomi Kobayashi; Department of Chemistry, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, JAPAN; **Ozone Modification on Surface of Polystyrene Derivatives**

Toshio Ogawa; Yuusuke Kimoto, Tohru Kimura and Atsuhiko Ishikawa; Kanazawa Institute of Technology, Ohgigaoka 7-1, Nonoichi, Ishikawa, 921-8501, JAPAN; **Surface Modification of Polypropylene by Flame Treatment with Silicon Compound**

S. Temmel, Ch. Buchgraber, W. Kern; Polymer Competence Center Leoben GmbH, A-8700 Leoben, AUSTRIA; **Improvement of Surface Properties of Polymers Modified by Photo-induced Processes**

T.Tanaka, **K.Vutova**, G.Mladenov, T.Takagi; Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko Shosse, 1784 Sofia, BULGARIA; **Surface Modification of Plastic Films by Charged Particles**

PLASMA TREATMENT

E. Steven Brandt and Jeremy Grace; Imaging Materials & Media R&D, Eastman Kodak Co., Rochester, NY 14650-2022; **Initiation of Atomic Layer Deposition on Polymer Surfaces by Plasma Pretreatment**

C. Canal, R. Molina, N. Carneiro, A.P. Souto, E. Bertran and P. Erra; Institute of Chemical and Environmental Research of Barcelona, Consejo Superior de Investigaciones Científicas, c/Jordi Girona 18-26, 08034 Barcelona, SPAIN; **Surface Modification of Plasma Treated Textiles by Dendrimer Application**

C. Canal, F. Gaboriau, I. Junkar, U. Cvelbar, N. Hauptman and A. Ricard; Laboratoire de Plasmas et de Conversion d'Énergie (LAPLACE), Université Paul Sabatier, 118 Route de Narbonne Bat.3R2, 31062 Toulouse, FRANCE; **Ar-CF₄ Plasma Post-discharge Treatment of Natural and Synthetic Polymer Fibres**

I. Hudec, M. Jaššo, **M. Cernák**, L. Cernáková and H. Krump; Institute of Physics, Comenius University, Bratislava, SLOVAKIA; **Adhesion Strength Study Between Plasma Polymerized Polyester Cords and a Rubber Matrix**

J. Friedrich, R. Mix and J. Falkenhagen; Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, D-12205 Berlin, GERMANY; **Deposition and Characterization of Plasma Copolymerized Allyl Alcohol Adhesion Promoting Polymer Layers**

R. Molina, C. Canal, E. Bertran and P. Erra; Department of Optical and Applied Physics, University of Barcelona, 08028 Barcelona, SPAIN; **Atmospheric Plasma Treatments on Textile Materials**

J. Reece Roth; Dept. of Electrical & Computer Engr., 409 Ferris Hall, University of Tennessee, Knoxville, TN 37996-2100; **Polymer Surface Modification with a One Atmosphere Uniform Glow Discharge Plasma (OAUGDP)**

K.-D. Weltmann, J. Ehlbeck, R. Brandenburg, T. V. Woedtke, U. Krohmann, M. Stieber, K. Rackow, E. Kindel and R. Foest; Institute of Low Temperature Plasma Physics (INP), Felix-Hausdorff-Straße 2, 17489 Greifswald, GERMANY; **Polymer Surface Decontamination of Heat-Sensitive Goods Using Low Temperature Plasma Technology**

Rory A. Wolf; Enercon Industries Corporation - Surface Treatment, Induction Sealing, & Power

Supply Technologies, W140 N9572 Fountain Blvd., Menomonee Falls, Wisconsin 53051; **Advances in Adhesion with CO₂-Based Atmospheric Plasma Surface Modification**

NEW AND INNOVATIVE TECHNOLOGIES

J. Friedrich, R. Mix, S. Wettmarshausen and A. Meyer-Plath; Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, D-12205 Berlin, GERMANY; **A New Concept of Adhesion Promotion in Metal-polymer Composites by Introduction of Covalently Bonded Hydrophobic Spacers at Interface**

E. T. Kang; Dept. of Chemical Engineering, National University of Singapore, Kent Ridge, SINGAPORE 119260; **Modification of Polymers via Surface-Initiate Living Radical Polymerizations**

Zheng Cao, **Jingxin Lei**, Jun Gao and Qiman Li; State Key Lab. Of Polymer Materials Engineering, Polymer Research Institute, CHINA; **Surface Modification of Polyolefine via A Novel Non-vapor and Non-liquid Photografting Method**

P. R. Norton, Natasha Patrino, Jessica McLachlan, Sarah Faria, Seyed Tadayyon, Claire McCague and Nils O. Petersen; Department of Chemistry, University of Western Ontario, London, ON, CANADA; **Novel Techniques for PDMS Surface Modification: Microscale Biocompatible Patterning and Robust Bonding**

Dae Up Ahn and **Erol Sancaktar**; Department of Polymer Engineering, The University of Akron, Akron, OH 44325-0301; **Control of Block Copolymer Cylinder Orientation by Homopolymer Blending**

Jay J. Senkevich; Carissa S. Jones and Young-Soon Kim; Brewer Science Inc., 2401 Brewer Dr., Rolla, MO 65401 USA; **Direct Electroless Metallization of a CVD Polymer Film Without a Catalytic Layer**

Frank Simon; Institute of Polymer Research, Hohe Straße 6, D-01069 Dresden, GERMANY; **Super-hydrophobic Aluminium Surfaces**

Grigoriy Kyryk and **Alexander Stadnick**; Ukrrosmetall Concern, 6 Kursky Avenue, Sumy, UKRAINE 40020; **Reception of Metal Coverings on Polymeric Materials By Methods of Conductors Electric Explosion**

BIOTECHNOLOGY APPLICATIONS

K. Opwis, **T. Bahnert** and E. Schollmeyer; Adlerstr. 1, 47798 Krefeld, GERMANY; **Surface Modifications for the Control of Cell Growth on Textile Substrates**

Arthur J. Coury; Genzyme Corporation, Cambridge, MA; **Achieving and Verifying Tissue Adherence to Assure Performance of Hydrogel-Based Medical Devices**

Wang Ke, Liang Hong, Zhao-Lin Liu; Department of Chemical and Biomolecular Engineering, National University of Singapore, BLK E5 02-02, 4 Engineering Drive 4, SINGAPORE 117576; **Developing a Substantially Thin Ni/P Layer on the Surface of Silicone Elastomer**

Carel Jan van Oss; Department of Microbiology and Immunology School of Medicine and Biomedical Sciences, University at Buffalo, North Campus, Buffalo, New York, NY 14214-300; **Surface Properties of Bacteria, Human Cells And Solid Substrata - Which Factors Cause Adhesion or Non-Adhesion to Prevail**

K. Schröder, B. Busse, H. Steffen, A. Ohl, A. Quade, K.-D. Weltmann; Institut für Niedertemperatur-Plasmaphysik e.V. (INP), Felix - Hausdorff - Str. 2, 17 489 Greifswald, GERMANY; **Plasma-Induced Generation of Cell-Adhesive and Cell-Repulsive Polymer Surfaces for Cell-based RNA Arrays**

INDUSTRIAL APPLICATIONS

Michel Grisel; URCOM Université du Havre, 25 rue Philippe Lebon, F-76058 LE HAVRE Cedex, FRANCE; **Polymer Surface Modification for Improvement of Adhesion Properties of Structural Composites Used in Aeronautics**

K. Opwis, T. Meyer-Gall, T. Textor, T. Bahnert, and E. Schollmeyer Deutsches Textilforschungszentrum Nord-West e. V., Adlerstr. 1, 47798 Krefeld, GERMANY; **Textile Catalysts - Immobilization of Organometallic Catalysts on Fibers**

Michael S. Silverstein; Department of Materials Engineering, Technion-Israel Institute of Technology, Haifa 32000, ISRAEL; **Surface Modification of Low-k Dielectrics**

ANALYTICAL EVALUATION

M. Ignat, C. Malhaire, G. Ravel and E. Quesnel; SIMAP INP Grenoble, FRANCE; **Cracking and Deadhesion of Thin Metal Films on Mechanically Modified Polymer Surfaces**

Graham J Leggett; Department of Chemistry, University of Sheffield, Brook Hill, Sheffield S3 7HF, UK; **Measuring Molecular Organisation at the Nanometre Scale: Surface Analysis by Friction Force Microscopy**

W. G. Mahy; Akzo Nobel Chemicals Research & Technology, THE NETHERLANDS; **Increasing the Performance of Polymer-Based Applications by Interphase Modification: Relevance of Microanalysis**

Andrew Nelson; ANSTO, New Illawarra Road, Menai, NSW 2234, AUSTRALIA; **The Role of Reflectometry Techniques in Examining Thin Polymer Film Compositions**

E. Metwalli, V. Körstgens and P. Müller-Buschbaum; Physik-Department, TU München, LS E13, James-Franck-Str. 1, 85747 Garching, Germany; **Evaluation of the Interfacial Adhesion Between a Model Pressure Sensitive Adhesive and Chemically Modified Surfaces Using the Probe Tack Method**

M. Charbonnier, F. Gaillard and **M. Romand**; Université de Lyon, Laboratoire des Sciences Analytiques, UMR-CNRS # 5180, Université Claude Bernard-Lyon 1, 43 Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, FRANCE; **Compared Catalytic Activity and Subsequent Electroless Metallization of Polymer Surfaces Treated by NH₃ and N₂ Plasma**

NANOSCALE INVESTIGATIONS

C. Lew, **F. Chowdhury**, **M. V. Hosur**, **A. N. Netravali**; Dept. of Fiber Science and Apparel Design, Cornell University, Ithaca, NY; **The Effect of Silica (SiO₂) Nanoparticle and Ethylene/Ammonia Plasma on the Carbon Fiber/NanoEpoxy Interfacial Shear Strength**

Dae Up Ahn and **Erol Sancaktar**; Department of Polymer Engineering, The University of Akron, Akron, OH 44325-0301; **Direct Fabrication of High Density Polymer or Silicon Nano-Dots by Excimer Laser Irradiation on Block Copolymer Masks**

M. Krysak, A. Jayasekar, B. Parekh, T. Debies, K. S. V. Santhanam, R. A. DiLeo, B. J. Landi, R. P. Raffaele and **G. A. Takacs**; Department of Chemistry, Center for Materials Science and Engineering, Rochester Institute of Technology, Rochester, NY, 14623; **Gas-Phase Surface Functionalization of Carbon Nanotubes with UV Photo-Oxidation**

Terrence Vargo, David MacRae, and Derrick Lucey; Integument Technologies, Inc., 72 Pearce Avenue, Tonawanda, NY 14150; **Plasma Surface Modification Meets Nanotechnology**

PRELIMINARY PROGRAM SIXTH INTERNATIONAL SYMPOSIUM ON SILANES AND OTHER COUPLING AGENTS
To be held June 13-15, 2007; University of Cincinnati, Cincinnati, Ohio, USA

This symposium continues the tradition set by the first symposium in this series: "Silanes and Other Coupling Agents" which was hosted in 1991 by the Dow Corning Corporation in honor of Dr. Edwin P. Plueddemann. As with its predecessors, this symposium will be concerned with the technological areas where the use of surface primers such as silanes is critical to the success of many technologies. It is also our distinct privilege to be able to hold this the sixth symposium in the series in collaboration with Prof. Wim van Ooij and his group at the University of Cincinnati. Prof. van Ooij was a participant at the 1991 symposium in honor of Dr. Plueddemann and has been an active researcher in the field of silanes ever since. Prof. van Ooij and his group look forward to hosting this symposium and greeting all participants from both academia and industry from all corners of the globe. Historically the silanes have been used as coupling agents for thin films in the microelectronics industry and in glass fiber composites where the use of silanes has been an enabling factor in the success of many manufactured products. Quite surprisingly, silanes have also found a role in biotechnology as specific coupling agents for bonding polynucleotides to the so-called "gene chips" and also in cosmetic applications. This symposium is organized to bring together scientists, technologists and engineers interested in all aspects of coupling agent technology, 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. The invited speakers have been selected so as to represent widely differing disciplines and interests, and they hail from academic, governmental and industrial research laboratories. This meeting is planned to be a truly international event both geographically and scientifically. **NOTE** this is not a complete listing of papers to be presented and the address given may apply only to the presenting author.

SILANES IN COMPOSITES

Khodzhaberdi Allaberdiev; Ukraine State Scientific Research Institute for Plastics, Illicha

pr.,97, Donetsk,83059, UKRAINE; **Investigation of the Interphase Epoxy Composites**

M. Masudul Hassan, and **Mubarak A. Khan**; Radiation and Polymer Chemistry Lab., Institute of Nuclear Science and Technology Bangladesh Atomic Energy Commission, P. O. Box 3787, Dhaka, BANGLADESH; **Role of Amino-Silane on the Mechanical Performance of the Jute-Polycarbonate Composites**

Jukka P. Matinlinna, Jon E. Dahl, Stig Karlsson, Lippo V. J. Lassila and Pekka K. Vallittu; NIOM – Nordic Institute of Dental Materials, P.O.Box 70, NO-1305 Haslum, NORWAY; **The Effect of the Novel Silane System to the Flexural Properties of E-glass Fiber-Reinforced Composite**

SILANES AS SURFACE MODIFICATION AGENTS

Barry Arkles and Youlin Pan; Gelest Inc., 11 East Steel Rd., Morrisville, PA 19067; **Hydrophobicity, Hydrophilicity and Silane Surface Modification**

T. Textor, **T. Bahners**, F. Schroeter and E. Schollmeyer; Deutsches Textilforschungszentrum Nord-West e. V., Adlerstr. 1, 47798 Krefeld, GERMANY; **Sol-gel-coatings Filled with Doped Tin Oxide Nanoparticles for Textiles with Modified Absorption and Reflection Properties**

E. T. Kang; Dept. of Chemical Engineering, National University of Singapore, Kent Ridge, SINGAPORE 119260; **Silane Coupling Agents for Surface-initiated Living Radical Polymerizations**

Carl Tripp; Laboratory for Surface Science & Technology, Engineering and Science Research Building, University of Maine, Orono, ME 04469; **The Use of Supercritical CO₂ for Conducting Silane Reactions on Surfaces**

NOVEL APPLICATIONS AND COUPLING AGENTS

Peter Beentjes; Corus RD&T, P.O.Box 10.000, 1970 CA Ymuiden, THE NETHERLANDS; **On the Barrier Properties of Siloxane Coatings Based on Flexible Silane Precursors**

H. T. Deo; Polygel Technologies India Private Limited, Fort, Mumbai, INDIA; **Coupling Agents in Chelating Chemicals, Printing Inks, Silicon Emulsions and Paint Adhesive Formulations**

R. De Palma, S. Peeters, W. Laureyn, G. Borghs, C. Van Hoof, G. Maes; Interuniversity

Microelectronics Center (IMEC), BELGIUM; **How to Tune the Functionality of Magnetic Nanoparticles Using Silanes?**

Stephen L. Kaplan; 4th State, Inc., 1260 Elmer Street, Belmont, CA 94002; **Plasma Silanization of Metals, Ceramics and Polymers**

Burkhard Standke, Björn Borup, Peter Jenkner, and Christian Wassmer, Degussa GmbH, Rheinfelden, GERMANY; **VOC Free Multifunctional Organosilane Systems - A New Modular Concept for Water Borne Sol-Gel Coatings**

T. Textor, F. Schroeter and E. Schollmeyer; Deutsches Textilforschungszentrum Nord-West e. V., Adlerstr. 1, 47798 Krefeld, GERMANY; **Photocatalytic Titania Derived by Sol-Gel-Technique for Textile Application**

SILANE SURFACE THERMODYNAMICS

V. Cech, S. Lichovnikova, J. Sova, and J. Studynka; Institute of Materials Chemistry, Brno University of Technology, Brno, CZECH REPUBLIC; **Surface Free Energy of Silicon-Based Plasma Polymer Films**

Ramsey Hamade; American University of Beirut, 850 Third Avenue 18th floor, New York, NY 10022; **Durability of Silane-Modified Adhesive Bonds**

X. Liu, J. L. Thomason and **F. R. Jones**; Department of Engineering Materials, University of Sheffield, Sheffield, S1 3JD, UK; **The Concentration of Hydroxyl Groups on Glass Surfaces and Their Effect on the Structure of Silane Deposits**

SILANES AS CORROSION INHIBITORS

F. Deflorian, S. Rossi, M. Fedel and L. Fedrizzi; Dipartimento di Ingegneria dei Materiali e Tecnologie Industriali, Università di Trento, Via Mesiano 77, 38050 Trento, ITALY; **Advanced Electrochemical Techniques for Studying Silane Based Pretratments as Adhesion Promoters on Different Metals**

Ji-Ming Hu, Wei-Gang Ji, Liang Liu, Jian-Qing Zhang and Chu-Nan Cao; Department of Chemistry, Zhejiang University, Hangzhou 310027,

P. R. CHINA; **Improving the Corrosion Performance of Epoxy Coatings by the Modification with "Active" and "Non-Active" Silane Monomers**

A. N. Khramov, L.S. Kasten, V. N. Balbyshev and J. A. Johnson; Universal Technology Corp., 1270 N. Fairfield Rd., Dayton, OH 45432-2600, USA; **Phosphonate-Functionalized Sol-Gel Surface Treatments for Aluminum and Magnesium Alloys**

Paula Puomi, Zhangzhang Yin, Wim J. van Ooij, Akshay Ashirgade and Anuj Seth; University of Cincinnati, 560 Engineering Research Center Cincinnati, OH 45221-0012; **Novel Chromate-Free Silane-Containing Superprimer Technology**

Dale W. Schaefer; Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45208; **The Role of Silane Coupling Agents in Metal-Protective Films**

W. J. van Ooij; Dept. of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH 45221-0012; **Overview of Potential of Silanes to Protect Metal Against Corrosion Phenomena**

Zhangzhang Yin, Akshay Ashirgade, Anuj Seth, Paula Puomi and Wim J van Ooij; Department of Chemical and Materials Engineering, Cincinnati, OH 45221; **Zinc Phosphate as an Effective Anticorrosion Pigment in Silane-based Waterborne Primers**

Qingsong Yu; Department of Chemical Engineering, Center for Surface Science and Plasma Technology, University of Missouri-Columbia, Columbia, MO 65211; **Plasma Polymer Coatings in Corrosion Protection of Metallic Materials**

SILANE SURFACE CHARACTERIZATION

X. M. Liu, J. L. Thomason and F. R. Jones; 1) Department of Engineering Materials, University of Sheffield, Sheffield, S1 3JD, UK; **XPS and AFM Study of the Structure of Hydrolysed Aminosilane on E-glass Surfaces**

Anthony A. Parker, Todd Wagler and Peter Rinaldi; A. A. Parker Consulting & Product Development, Newtown, PA; **Solid State NMR Studies of Surface Adsorbed Molecules on Inorganic Pigments**

Peng Wang, Bill Hamilton and **Dale W. Schaefer**;

Dept. of Chemical and Materials Engineering, Univ. of Cincinnati, Cincinnati, OH 45221;

Characterization of Hydrothermal Degradation of Organosilane Films on Silicon Wafer by Neutron Reflectivity

R Raval, **S J Shaw** and G Woods; Defence Science and Technology Laboratory, Salisbury, UK;
Spectroscopic Probing of Model Silane Coupling Compounds at Model Surfaces

Peng Wang and Dale W. Schaefer, Dept. of Chemical and Materials Engineering, Univ. of Cincinnati, Cincinnati, OH 45221;

Characterization of Epoxy-Silane Films by Combined Scattering Techniques

Wisconsin 53726-2398; **Surface Modification of Wood by Alkoxysilane Sol-gel Deposition to Create Anti-mold and Anti-fungal Characteristics**

L. Ge, S. Sethi, Betul Yurdumakan, P. M. Ajayan and **A. Dhinojwala**; Department of Polymer Science, University of Akron, Akron, OH;
Synthetic Gecko Foot-hairs from Multiwalled Carbon Nanotubes

Ezzeldin Metwalli; Physikdepartment E13 , Technische Universität München James-Franck-Straße 1, D-85747, Garching , GERMANY; **Aminosilane treated glass substrates for DNA microarrays**

SILANES IN BIOTECHNOLOGY

Mandla A. Tshabalala, Vina Yang and Ryan Libert; USDA Forest Service, Forest Products Laboratory, One Gifford Pinchot Drive, Madison,

REGISTRATION INFORMATION

DATES:

June 11-13, 2007: SIXTH INTERNATIONAL SYMPOSIUM ON POLYMER SURFACE MODIFICATION: RELEVANCE TO ADHESION

June 13-15, 2007: SIXTH INTERNATIONAL SYMPOSIUM ON SILANES AND OTHER COUPLING AGENTS

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Duration: 1 day

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