

SurFACTS in *Biomaterials*

Summer 2014
Volume 19, Issue 3

Surfaces in Biomaterials Foundation Announcements

Stay Up-to-Date with the Surfaces in Biomaterials Foundation on Twitter and LinkedIn

Twitter: @SurfacesIBF

LinkedIn: Surfaces in Biomaterials Foundation Group

SIBF has launched a Twitter feed and can be followed at @SurfacesIBF. The feed provides a great way to keep in touch with events for the Foundation and news in the biomaterials in field. The SIBF group on LinkedIn also continues to be active and provides another venue to network with surface science professionals and stay in touch with the field.

Thanks to Jakub Truty for organizing the LinkedIn page and Twitter feeds. Jakub recently graduated with his M.S. in Biomedical Engineering from Cal Poly and is currently working with Abbott Laboratories in their Professional Development Program.

Open House Rescheduled for September 11

The SIBF open-house originally scheduled for June 23 has been moved but will still be occurring at NAMS from 5-8 pm on Thursday, September 11.

Webinars

The SIBF webinar series is being revived. The first webinar will be presented by APS on Thursday, August 21st at 11 am Central time. For more information please visit the Sponsor a Webinar link under the Conferences and Events tab on the SIBF website.

Early Bird Rates End August 1

SURFACES IN BIOMATERIALS FOUNDATION
BIOINTERFACE 2014
OCTOBER 6-8, 2014 REDWOOD CITY, CA

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Members are encouraged to submit articles for future editions of SurFACTS. Please e-mail your report (with all appropriate figures and graphics) to Staff Editor Jazzy McCroskey at jasperm@ewald.com for consideration in a future issue. Deadlines for upcoming issues are posted on surfaces.org.

Member News

In major news for Surfaces in Biomaterials members, **Medtronic** announced the intended acquisition of Covidien in June for \$43 billion. In addition to expanding its product portfolio, this deal will also provide significant tax benefits to Medtronic. In device news, Medtronic published results in The Lancet showing superior outcomes with Type 2 diabetes for insulin pumps compared to daily injections. In another publication in the New England Journal of Medicine, it was shown that insertable cardiac monitors detect atrial fibrillation in stroke patients better than standard care. Medtronic submitted final data to the FDA for its IN.PACT Admiral drug-coated balloon for peripheral artery disease and expects approval in early 2016.

Boston Scientific received CE Mark for its Ranger™ drug coated balloon in July. The device features TransPax™ coating technology to deliver paclitaxel for peripheral vascular disease. The company presented promising data on its Lotus™ valve and SYNERGY™ stent systems at Euro PCR in May. Boston Scientific also announced acquisitions of the interventional division of Bayer AG focused on peripheral intervention and IoGyn, Inc a new technology to treat uterine fibroids.

AST Products, Inc. unveiled its newest medical product, Ioli, at the American Society of Cataract and Refractive Surgery's annual meeting in Boston in April. Ioli is an intraocular lens delivery system that uses AST's LubriMATRIX™ technology to protect the lens during cataract surgery.

ExThera Medical received an issued patent related to its Seraph® Microbind® affinity blood filter designed to treat blood stream infections.

American Preclinical Services (APS) passed an FDA audit of its quality systems in March. APS also presented on methods for thrombogenicity testing at an FDA public workshop in April. Links to the presentation and the FDA workshop program are available on the APS website. In June, APS published in JACC on using ultrasound to assess lumen gain and pulsatility of coronary arteries implanted with bioresorbable drug eluting vascular scaffolds.

St. Jude Medical announced a deal to acquire NeuroTherm for around \$200 million. NeuroTherm makes devices to treat spinal pain using radiofrequency ablation. The company's Nanostim™ leadless pacemaker

was honored as most innovative product at the Cardioslim 2014 meeting. St. Jude received FDA approval for the CardioMEMS heart failure management system which monitors pulmonary artery pressure in patients discharged from the hospital and transmits data to their healthcare provider. It also announced the first implants of the Portico™ aortic heart valve in its US IDE trial.

Biocoat launched a new website promoting reproductive technology. The website is designed to promote the HBA® and PICS® tests which help quantify and select mature sperm based on binding affinity to Hyaluronan. President and CEO Keith Edwards also published an article in Medical Device Developments and a column in Issues in Pharmaceuticals Technology.

CSIRO secured a deal with Boron Molecular to manufacture and sell RAFT chain transfer agents for R&D and commercial purposes. This move is expected to increase uptake of the technology by providing large scale quantities of the reagents for improved polymer synthesis.

Bausch and Lomb presented 22 posters and sponsored one oral presentation at the ARVO annual meeting in May. Presentations covered topics ranging from pharmaceuticals for glaucoma treatment to novel contact lens materials. The company also received FDA clearance in June for the Biotrue® ONEday for Presbyopia lens. This lens is a one-day disposable lens featuring 3-Zone Progressive™ design, along with bio-inspired HyperGel™ material.

Covidien launched several next generation products in the US and Europe including the Trellis™ peripheral infusion system and the Pipeline™ Flex device for aneurysm treatment. The TRELLIS system provides pharmacomechanical thrombolysis to treat blood clots. The PIPELINE FLEX offers a new delivery system for the endovascular flow diverter which makes the device easier to place and reposition. The company received FDA approval for the Apollo™ Onyx™ Delivery Micro Catheter for its liquid embolic system for treatment of brain arteriovenous malformations. Covidien also released 2-year results of the Stellarex™ Balloon with EnduraCoat™ technology for treatment of peripheral vascular disease. The results indicated that the coated balloon was safe with durable results in primary patency and target lesion revascularization.

Member News continues on pg. 3

CooperVision announced an agreement to acquire Sauflon Pharmaceuticals a European contact lens manufacturer and distributor. The deal will expand CooperVision's portfolio of daily disposable lenses.

Coatings2Go, an affiliate of Surface Solutions Laboratories, Inc., received ISO 13485 certification for worldwide distribution in May.

SurModics introduced a new non-corrosive, non-hazardous TMB stop solution as part of its in vitro diagnostic product offerings. The product provides an advantage to kit manufacturers due to decreased burdens for labeling and shipping as compared to

traditional corrosive stop solutions.

DSM awarded the 2014 DSM Materials Sciences Award to Professor Jian Ping Gong of the Faculty of Advanced Life Science at Hokkaido University in Japan. The award is presented in cooperation with IUPAC and honors Professor Gong's work on double-network hydrogels and materials science.

Peter Gabriele of **Secant Medical** was the keynote speaker at the Johns Hopkins University Annual Research Symposium in May. His talk was focused on the creation of next-generation regenerative medical devices.



2014 NESAC/BIO WORKSHOP

Surface Characterization of Biomaterials

Learn to Characterize Biomaterial Surface Composition and Structure

The National ESCA and Surface Analysis Center for Biomedical Problems (NESAC/BIO) is a state-of-the-art surface analysis center whose mission is the development and application of surface analysis methods for biomedical research.

This NESAC/BIO Surface Characterization Workshop includes lectures and surface analysis demonstrations. Demonstrations on NESAC/BIO instruments will provide application examples for the material covered in the workshop lectures. Attendees will learn the capabilities of surface analysis methods and how to intelligently review data received from surface analysis laboratories. The workshop will focus on the following methods:

- Electron Spectroscopy for Chemical Analysis (ESCA)
- Secondary Ion Mass Spectrometry (SIMS)
- Scanning Probe Microscopy (SPM)
- Sum Frequency Generation (SFG)
- Near Edge X-ray Absorption Fine Structure (NEXAFS)
- Multivariate Data Analysis
- Contact Angle Measurements
- Surface Modification
- Surface Plasmon Resonance



For More Information:

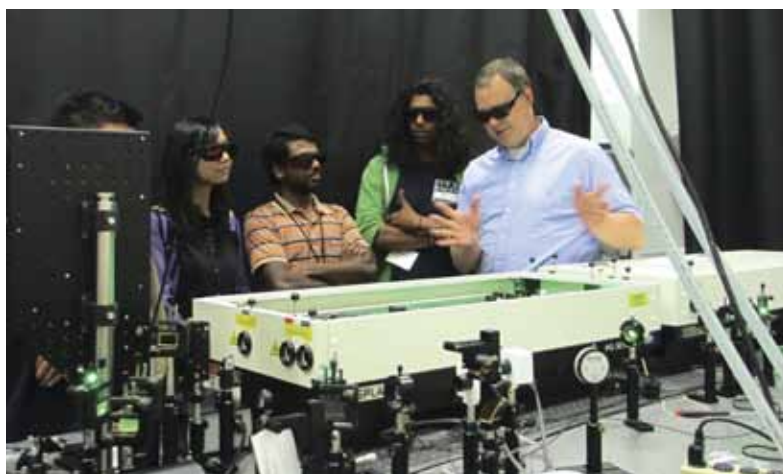
Endorsed by biomaterial.net

<http://www.nb.uw.edu/content/nescabio-workshop>

August 18 - 20, 2014

**National ESCA and Surface Analysis Center
for Biomedical Problems**

University of Washington, Seattle, Washington USA



NESAC/BIO is funded by NIBIB



Grant # EB002027

Special Surface Science Networking Open House- note new date!

9/11/2014

When:

NOTE NEW DATE: Thursday, September 11
5:00-8:00pm

Where:

NAMSA (Clinical and Consulting Office)
4050 Olson Memorial Highway
Suite 450
Minneapolis, Minnesota 55422



Poly (ϵ -caprolactone) Nanowire Surfaces Influence cellular Functionality

By Victoria Leszczak¹, Nathan Trujillo¹, Ketul C. Popat^{1,2}

¹ Colorado State University, Department of Mechanical Engineering

² Colorado State University, School of Biomedical Engineering

Why nanomaterials?

The extracellular matrix (ECM) of all tissues is a complex cellular environment consisting of proteins, proteoglycans, and other soluble molecules that constantly interact with neighboring cells. These elements that constitute the ECM of macroscale human tissues are on the micrometer and nanometer scale ¹. The ECM offers mechanical support, biochemical cues and biomechanical cues that are crucial for cell functionality. However, the ECM organization within each tissue varies and displays a variety of forms at different stages of development ². Developing and tailoring a favorable environment that mimics the complex, nanoscaled organization of native ECM is the most critical aspect of tissue engineering and one, which remains to be the most difficult.

Implants have a promising potential to restore the damaged elements within tissues while maintaining normal tissue function. However, these implants have significant limitations ³⁻⁴. The greatest shortcoming is poor tissue/biomaterial integration which may lead to biomaterial rejection and failure ⁵. An unmet need exists to advance implant surfaces to encourage healing as well as native tissue integra-

tion and regeneration. The motivation to use nanostructured surfaces as interfaces for implantable devices is driven by previous studies that have shown nanoscale materials affect cell behavior such as morphology, functionality and cellular interactions ⁶⁻⁸. Nanotopography may provide a valuable technique for guiding cell growth and differentiation.

Poly (ϵ -caprolactone) nanowire surfaces as an interface for biomedical implants

A novel solvent-free template synthesis technique was used for fabricating controlled arrays of high aspect ratio, substrate-bound nanowires from poly (ϵ -caprolactone), a biocompatible and biodegradable polymer. Template synthesis is a simple procedure, which provides a controlled approach for developing nanoscale polymer constructs for tissue engineering applications in solvent free conditions, which eliminates issues of toxicity. Structural architecture of the surfaces was evaluated using scanning electron microscopy (SEM) (Figure 1). These nanowire (NW) surfaces were then evaluated for use in a variety of applications, including cardiovascular and orthopedic.

Poly (ϵ -caprolactone) Nanowire Surfaces Influence Cellular Functionality continues on pg. 4

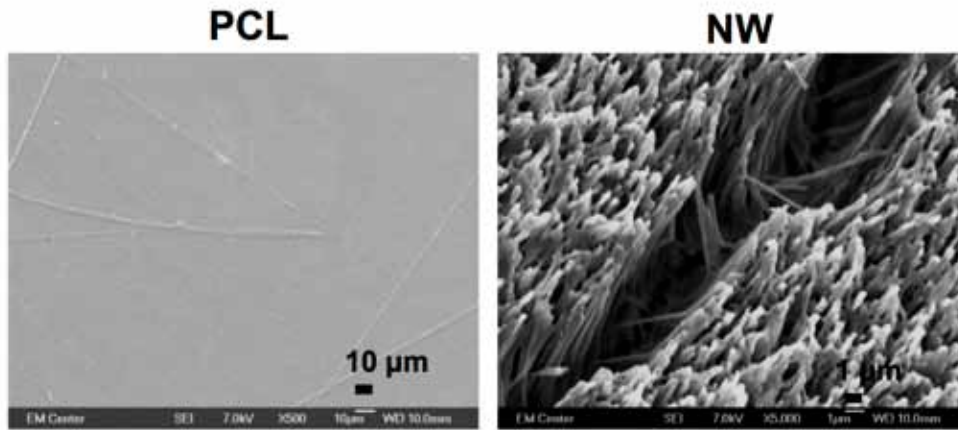


Figure 1. Representative scanning electron microscopy images of PCL and NW surfaces.

Poly (ϵ -caprolactone) nanowires as interfaces for cardiovascular implants

The surface properties of implantable cardiovascular devices are critical for long-term success of the implant. In particular, proper surface interactions with smooth muscle cells and the endothelium are vital. The response of human aortic smooth muscle cells and human microvascular endothelial cells (ECs) to control polycaprolactone (PCL) surfaces and NW

surfaces were investigated.

SMC and EC interaction with NW surfaces was investigated in terms of adhesion, morphology and differentiation. In these studies, SMCs and ECs exhibited increased adhesion on NW surfaces compared to PCL surfaces. SMCs and ECs displayed a more elongated body and low shape factor/high elongation factor on NW surfaces compared to smooth surfaces PCL surfaces.

Immunostaining and western blotting for key SMC and EC markers evaluated the differentiation potential of NW surfaces, indicating an increase in endogenous protein expression on NW surfaces (Figure 2).⁹⁻¹⁰

The results of these studies suggest the improved biocompatibility of polycaprolactone NW surfaces. The findings have shown improved EC and SMC functionality on NW surfaces. This research has promising implications with respect to the use of NW surfaces as interfaces for cardiovascular implants.

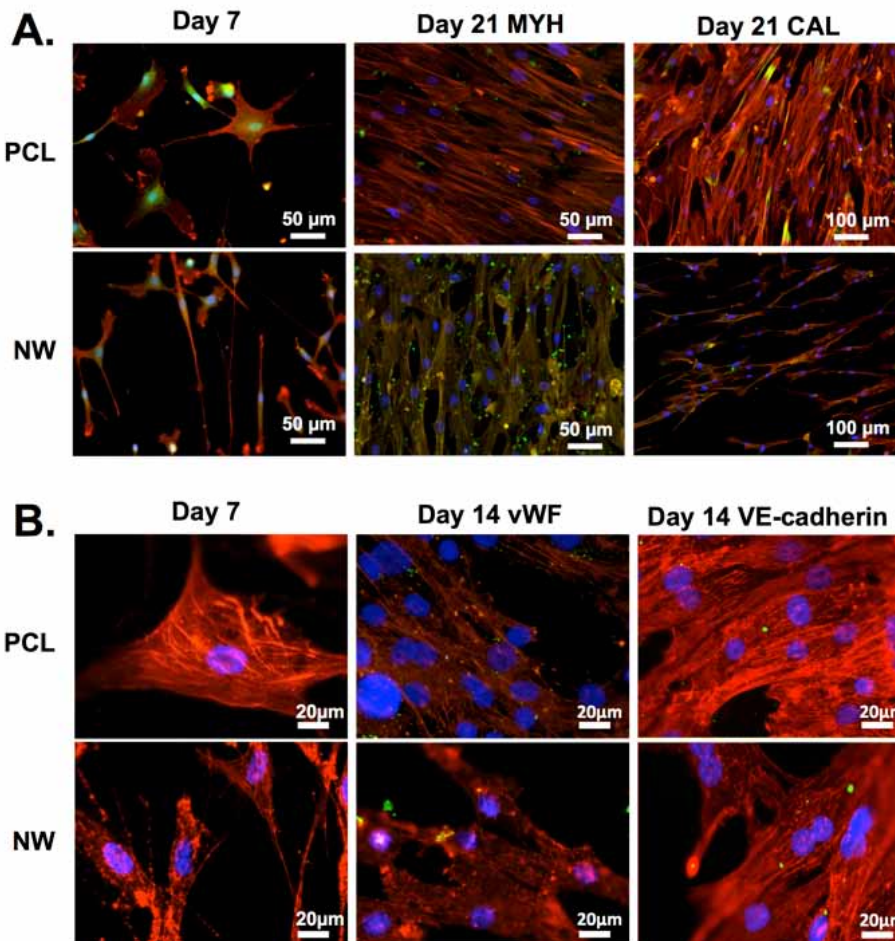


Figure 2. (A.) Representative fluorescence microscopy images of SMCs adhered on PCL and NW surfaces after 7 days of culture (left). Representative fluorescence microscopy images of SMCs on PCL and NW surfaces immunostained for heavy chain myosin (middle) and calponin (right) (green), actin (red) and nucleus (blue) after 21 days of culture. (B) Representative fluorescence microscopy images of ECs adhered on PCL and NW surfaces after 7 days of culture (left). Representative fluorescence microscopy images of ECs on PCL and NW surfaces immunostained for von Willebrand Factor (middle) and VE-cadherin (right) (green), actin (red) and nucleus (blue) after 14 days of culture.

Poly (ϵ -caprolactone) nanowires as interfaces for orthopedic implants

Autografts and allografts are widely used for bone graft procedures, yet they have numerous challenges to overcome and significant limitations. The procurement of autografts is limited with respect to morbidity and obtainable quantities, while allografts induce an immune response leading to the risk of rejection and the transmission of diseases¹¹. A synthetic grafting material such as poly (ϵ -caprolactone), may eliminate these dangers. Stem cells, which are able to differentiate down multiple cellular pathways, have been utilized to assess bone synthetic scaffolds. The response of adipose derived stem cells (ADSCs) to control PCL surfaces and NW surfaces was investigated.

The results indicate that the NW surfaces exhibited lower ADSC adhesion and proliferation as compared to PCL surfaces (Figure 3). However, the morphology of ADSCs were visibly different amongst the two surfaces, as NW surfaces displayed an elongated cell body with filopodia interacting with the modified surfaces. Despite the fact that both surfaces expressed alkaline phosphatase activity for up to 3 weeks of culture in osteogenic conditions, NW

surfaces expressed significantly higher osteocalcin (OC) and osteopontin (OP) expression compared to PCL surfaces (Figure 3). Overall, the results presented here indicate that the topography of the NW surfaces have a significant influence on the behavior of ADSCs.¹²

Summary

In conclusion, altering the topography of a scaffold surface to mimic the hierarchy of natural tissue has an incredible influence on cellular behavior. A novel solvent-free template synthesis technique was used to create substrate-bound NW from poly (ϵ -caprolactone). These NW surfaces were then evaluated in vitro for use in cardiovascular and orthopedic applications. The results indicate that NW surfaces produce an enhanced cellular response compared to control PCL surfaces.

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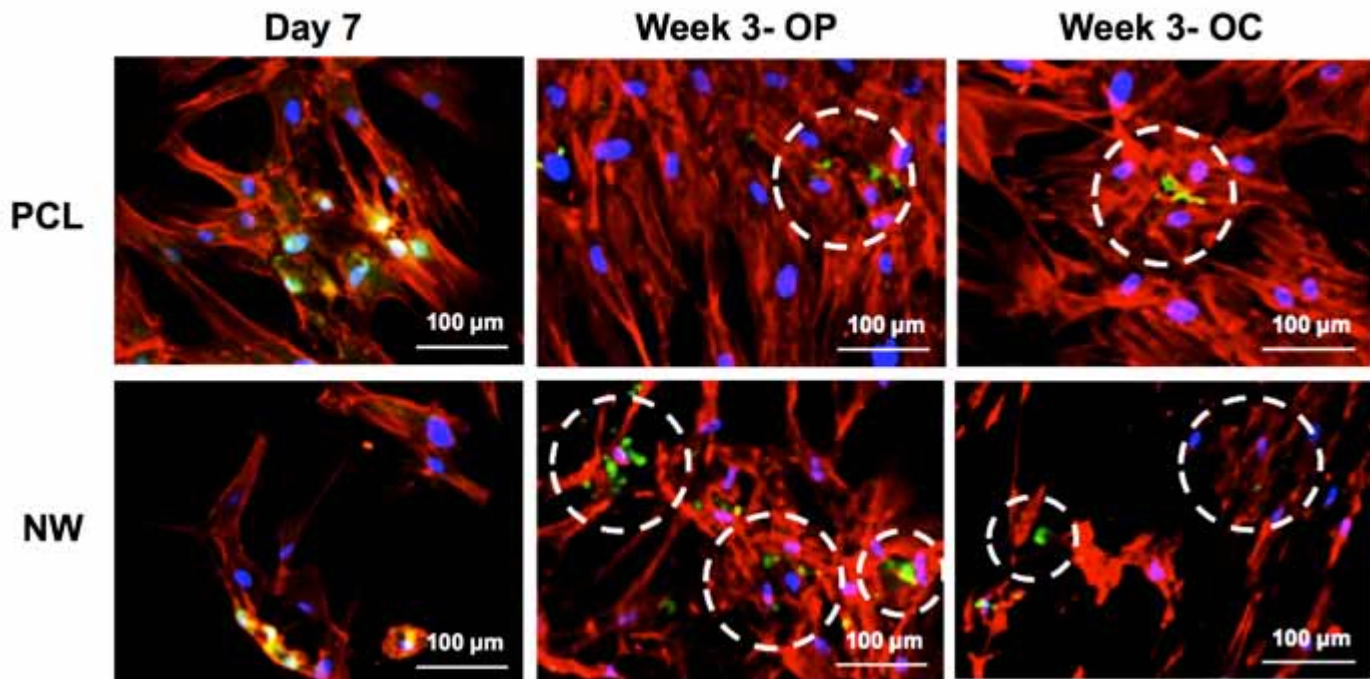


Figure 3. Representative fluorescence microscopy images of ADSCs adhered on PCL and NW surfaces after 7 days of culture (left). Representative fluorescence microscopy images of ADSCs on PCL and NW surfaces immunostained for osteopontin (middle) or osteocalcin (right), actin (red) and nucleus (blue) after 3 weeks of culture in osteogenic conditions. Circles indicate the location of FITC-labeled osteopontin or osteocalcin respectively (right).

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Patenting Around the World

By Colin Fairman

As some of you readers know, the U.S. recently passed laws to more closely align our patent system with the rest of the world, also known as the America Invents Act (AIA) (see this column Winter 2012). The most prominent part of the AIA is that the U.S. is now on a “first to file” regime like most other countries in the world. For those considering a global patenting strategy, however, there are still significant differences between countries that should be considered as well. This column will provide a brief comparison of patent regimes in the U.S. with countries globally and what filers need to consider when pursuing global IP protection.

Major factors to consider:

- Return on investment
- Geographic needs/requirements
- Scope of protection desired
- Cost of filing and prosecution
- Rigor of prosecution
- Quality of protection

Return on investment

Knowing what you want your return on investment (ROI) to be is the most important single criteria to consider when filing a patent application. All of the other factors listed above, contribute to your ROI. Furthermore, when considering your ROI, the applicant must also remember that the life of a patent is 20 years. Therefore, there is a certain amount of fortune telling needed to anticipate what your market is globally, how that market may change over the life

of the patent, and what your competitors may do during that time.

Geographic needs/requirements

With the ROI in mind, one next needs to consider which countries to file in. If the client wants global protection, identifying countries that have the desirable market is the most important consideration. In addition, an important consideration is infringing activity. Is it important to protect your invention in countries where you do not have a current market? If protection only in the U.S. is desired, then of course filing a U.S. utility application is all that is necessary. If protection in Europe or other countries is desired a global application under the Patent Cooperation Treaty (PCT) should be considered. There are 147 parties to the PCT allowing a single filing to enter national phase in any signatory country. This is where a little forethought regarding costs comes in. There has been a lot of discussion about the change to a “first to file” (with grace) regime in the U.S. under the AIA and how that alters strategies for filing. In reality the ability to protect your invention has not changed that much, because most frequently filed-in countries have still more restrictive filing criteria than the U.S. For example, while the U.S. is now a “first to file” country, a one year grace period exception is made for publications that disclose an invention, this exception is only for the U.S. Other important countries globally, regard any public disclosure, before the filing of a patent application as a bar to patentability. Further, the publication exception is only applicable to the sufficiency of the disclosure in the published

document. Determining how sufficient a disclosure in a scientific publication needs to be to provide broad patent coverage is still to be litigated (as it will certainly be). Consequently, there is still clearly no substitute to filing a provisional application.

The filing of a provisional application will allow the inventor to claim priority to that document both nationally and throughout the PCT. Further, because a provisional patent application is not peer-reviewed, such as a scientific paper is, the provisional application can be embellished to allow for more robust patent protection with the filing of a utility application within a year. In reality, if a publication has been prepared, there is little further effort required to turn the publication into a competent provisional application. In this respect, the cost for filing a provisional application (\$260/\$130) is insignificant compared to the protection that is provided by it. The flip side of the new AIA “first to file” regime is perhaps more important than “first to file” or publication with one-year grace, because the U.S. is no longer a first to invent country, there will no longer be an ability to show prior invention or to swear behind prior art disclosures. This is a significant change in the status quo for traditional U.S. prosecutors. In addition, with the elimination of first to invent regime the patent office will no longer have to resort to interference proceedings to determine which party, in a dispute over inventiveness, has priority to an invention. Of course, your need for geographic protection is also driven by the technological field you are engaged in. For example, big pharma tend to file in most large jurisdictions, while many high tech companies file only in countries that have high tech industry.

Scope of Protection

While the PCT provides a vehicle for obtaining patent protection globally, it does not alter the variance of what is considered patentable subject matter in signatory regimes. For example, business methods are patentable in Japan and to some extent in the U.S., Canada and Australia, but they are not patentable in Europe, India and many other countries. Similarly, GMOs, treatment of the human body, and human genes are variably patentable throughout the countries of the PCT. In the U.S. recent Supreme Court decisions limit the patentability of genes per se but did identify patentable subject matter and a means of claiming it. (Myriad, 2013, isolated, native, genes were not patentable, but the same gene identified in a non-naturally occurring form was patentable (e.g., cDNA or a portion of the gene in a vector). Inventions for methods of treating the human body are per se not patentable in most parts of the world (Europe, China, India and Japan), yet they are patentable in the U.S. However, in many of these cases claims may be re-written as “second use” claims or protection can be gained for the apparatus that makes the diagnostic or prosthetic device.

Cost of Global Filing

Patent filing costs vary per jurisdiction. Interestingly, some small commercially non-significant countries have quite high filing costs while other, larger markets, are more reasonable. In addition, foreign filing often requires translation into a country's national language. These fees can rapidly add up. Filing fees, alone, in Europe total approximately \$5,600.00. Further, once a patent is allowed in the European Patent Office it has to be validated

SurFACTS in Biomaterials is the official publication of the foundation and is dedicated to serving industrial engineers, research scientists, and academicians working in the field of biomaterials, biomedical devices, or diagnostic research.

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in each country where the owner wants the patent enforced. In France, Germany, Luxembourg, Monaco, Switzerland/Liechtenstein and the United Kingdom, no translation of the specification of the European patent needs to be supplied. In all other countries a translation of the specification needs to be supplied, adding to the overall cost. In addition, validation fees range anywhere from 280 to 600 €. When one compares the approximately \$9,000 total fees through prosecution in the U.S., to the \$92,000 (filing and added fees, validation costs, and annuities) for six European countries (FR, DE, IT, ES, CH) one realizes the importance of choosing target countries wisely. A similar application filed in Japan or China will cost approximately \$30,000 and \$17,000 respectively. It should also be remembered that the costs cited here constitute only the fees that are required by national patent offices. The costs of preparing responses to office actions, and attorney fees for filing the necessary documents are not included.

Requirements for Prosecution

I previously wrote about the requirements for enablement and written description, and the sufficiency of disclosure needed to support the claims of an application (Summer 2012). In a global context, the requirements for support of claims are enforced more or less stringently from country to country. While the patent system rests on a requirement that an application cannot be updated, once it is filed, different countries enforce this requirement more or less stringently. For example, those prosecuting patent applications in the U.S. have been able to bolster support in a specification by bringing in new data or information by way of a 1.132 Declaration. Further, prior to the enactment of the America Invents Act, it was quite easy to put new, supporting data in front of the examiner via a 1.131 declaration made by an inventor. Now, with the “first to file” regime, 1.131 declarations appear restricted to reexaminations. Similarly, 1.132 declarations were used to show knowledge by those of skill in the art in overcoming rejections made by examiners on what was known by those of skill “at the time the invention was made.” The patent rules now also reserve 1.132 declarations for reexamination. However, given that past practice had allowed a relative ease in presenting new information to the examiners, it is possible that examiners will still allow these types of evidence

to be put before them.

Europe has stricter guidelines regarding proffering evidence and/or data not expressly provided in a patent specification. In general, the EPO may allow presentation of information/data developed after the filing of a patent specification germane to specific claims.

Japan, China and Korea have even stricter guidelines than Europe. Generally, these countries do not allow presentation of data/information not expressly provided in the specification. Japan may allow the presentation of such data if it was collected prior to the filing of the patent application. China, as a general rule, does not allow the presentation of any data or subject matter that is not expressly taught in the “as-filed” application.

Consequently, the scope of allowable subject matter is generally much greater in the U.S. because the examiner may allow broader subject matter. For example, a U.S. examiner may allow claims to a “metal” widget where the specification teaches a molybdenum or tantalum widget. However, the Chinese examiner will only allow claims for a molybdenum or tantalum widget.

Quality of Protection

The strength or quality of the protection you will get for your invention when filing in foreign jurisdictions is the last subject to consider. A entire legal industry has been built up in the U.S. in the pursuit of enforcing patents or in showing that asserted patents may not be enforceable. As we all know, damages for infringing commercially successful patents may range in the millions to hundreds of millions of dollars.

Under the European patent convention, any infringement of a European patent is dealt with under national law. Therefore, the remedies available to patent holders and infringers will vary from country to country depending on each country’s posture regarding patents, litigation, and damages. However, because the judicial system in most of the EU states is relatively robust, the patent holder can have some expectation of a fair and transparent judgment on its merits.

Japan has a well-developed respect for patent rights and has two courts especially reserved for patent cases. However, in alleging infringement the patent owner must provide “specific conditions” of infringement in the complaint. Japan does not have

a system of discovery, therefore, a good deal of research must be made prior to filing any complaint for infringement in Japan. On the other hand, the special patent courts are assisted by full-time technical advisers selected from patent examiners and from patent attorneys, and in very complex issues the judges have a team of expert commissioners that can be called upon with advanced technical knowledge in the fields at issue.

China presents a conundrum as it has a vast potential market, yet patent law was only first recognized in China in 1985. This means that there is little appreciation by the general population that there may be specific penalties for copying or misappropriating technology, wherever it may be found. In addition, rather than having specific courts established to deal with patent law and technology issues, there are two completely separate ways to pursuing enforcement of patent rights in China. The first is through an administrative route at the local level. The second

is through judicial enforcement. For the administrative route, the Chinese State Intellectual Property Office (SIPO) has issued special guidelines for the local bodies to follow in an attempt to get more consistent actions in infringement cases. However, it is perhaps significant that one study showed that of the 937 infringement dispute cases received by local authorities in 2009 only 29 of those cases were instigated by foreign patent owners. The judicial route provides no procedure like the U.S. discovery process. Therefore, in instigating a case for infringement in the court system it is necessary to do most of the fact gathering prior to filing suit rather than after.

In summary, global patenting can be an expensive process. Careful considerations need to be made to determine the jurisdictions to file in based on the technology to be patented, the location of your competitors, and the location of your customers.



Registration now open! Early bird rates end August 1.

Surface Free Energy Analysis of Solid Matters

By Gang Pu, Ryan Farel and Dehua Yang, Ebatco

Abstract

Surface free energy is a key to understanding surface-related phenomena and is critically important in a number of biomedical applications such as coating, adhesion, wetting and lubrication. In this paper, we will discuss the concept and principles of surface free energy, its major theories and measurement techniques. Several examples of surface free energy analysis on solid matters are presented to highlight its useful applications.

Key words: Surface free energy, contact angle, work of adhesion, contact angle measurement.

Background on Surface Free Energy

Surfaces play an important role everywhere from people's daily life to the most advanced aerospace endeavor. The molecules at the surface lose half of their coordinates compared to those in the bulk. These surface molecules are pulled inward to minimize surface area. This asymmetrical environment makes the surface exist in a higher energy state. Such excessive energy is the origin of surface free energy for solids and surface tension for liquids. Surface free energy is thus key to understanding surface-related phenomena and it is critically important in a number of biomedical applications such as coating, adhesion, wetting and lubrication.

Although the term "surface free energy" for solids sometimes is considered an interchangeable term with "surface tension" for liquids, surface free energy does not have equal clarity as its counterpart. The surface tension of liquid has a clear definition as the work needed to increase a unit surface area and can be directly measured through pendent drop or capillary force methods. Solids cannot change their surface area without doing work against the elastic forces and plastic resistance, therefore the surface free energy of solids cannot be directly measured like liquids. The indirect methods and the corresponding theories always require one or more surfaces to interact with the surface of interest. Most popular theories are based on the Young-Dupré adhesion theory and contact angle measurements of different probe liquids to solid surfaces. To per-

form surface free energy analysis using the contact angle measurement approach, the surface tension values of the probe liquids are needed. Different probe liquids will have different interactions with the same surface. The contact angles are thus the interaction results between the solid surface and the probe liquids. Correlating the contact angle data with the known surface tension values of different probe liquids using the established models allows the total values and components of the surface free energy of the solid surface to be determined.

When a droplet of a probe liquid is deposited on a solid surface, there are competing interactions between cohesion of the liquid molecules and the adhesion between the liquid and the solid. If the work of adhesion between the solid and the liquid is higher than the work of cohesion of the liquid molecules, the liquid can completely spread over the solid surface. Otherwise, if the work of cohesion exceeds the work of adhesion, the liquid forms a finite contact angle on the solid based on Young's equation [1]. According to Young's equation as shown in Equation (1), the interfacial tension forces are balanced at the three-phase interface point for vapor (under the most of circumstances air), the liquid and the solid. This is shown in Figure 1, where θ is the contact angle, γ_s is the solid surface free energy, γ_L is the liquid surface tension, and γ_{SL} is the solid-liquid interfacial tension.

$$\gamma_s = \gamma_L \cos \theta + \gamma_{SL} \quad (1)$$

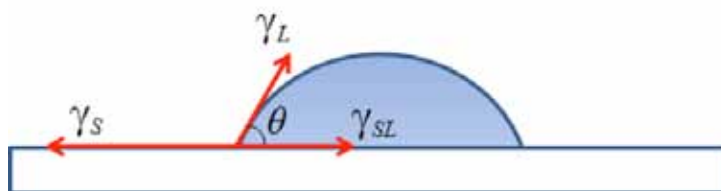


Figure 1. Interfacial tension components and contact angle of a liquid droplet on a solid surface.

Contact angle measurements have monolayer-detecting sensitivity and contact angle is the result of the interactions between the liquid and the solid. Therefore, contact angle analysis can reveal infor-

mation on the surface free energy of the solid. As a matter of fact surface free energy analysis through contact angle measurement represents a much less costly way compared with many other surface analysis methods.

Theories on Surface Free Energy Analysis Based on Contact Angle Data

Zisman theory is one of the simplest models for surface free energy analysis which was proposed by Zisman in early 1950s [2]. Zisman theory is an empirical connection between the cosine of the contact angle, θ , and the probe liquid surface tension, γ . Zisman, as well as many other researchers, observed that there was a tendency for contact angle on the same solid sample to decrease as liquid surface tension decreases. Zisman defined the surface free energy of a solid to be equal to the surface tension of the liquid with the highest surface tension (real or imaginary) that will completely wet the solid with a zero contact angle.

The measurements are usually performed with a series of probe liquids with known surface tension values. The contact angle of each liquid was measured and plotted as $\cos\theta$ vs liquid surface tension. The extrapolated value where $\cos\theta = 1$ is called the critical surface tension of the solid. The data plotted is called "Zisman-Plot". Figure 2 shows a Zisman-Plot for one tested sample. The tests were performed with five probe liquids including water, formamide, ethylene glycol, diiodomethane and 1-bromonaphthalene. The critical surface tension, from the extrapolated value of the linear data fitting, was 19.0 mJ/m^2 .

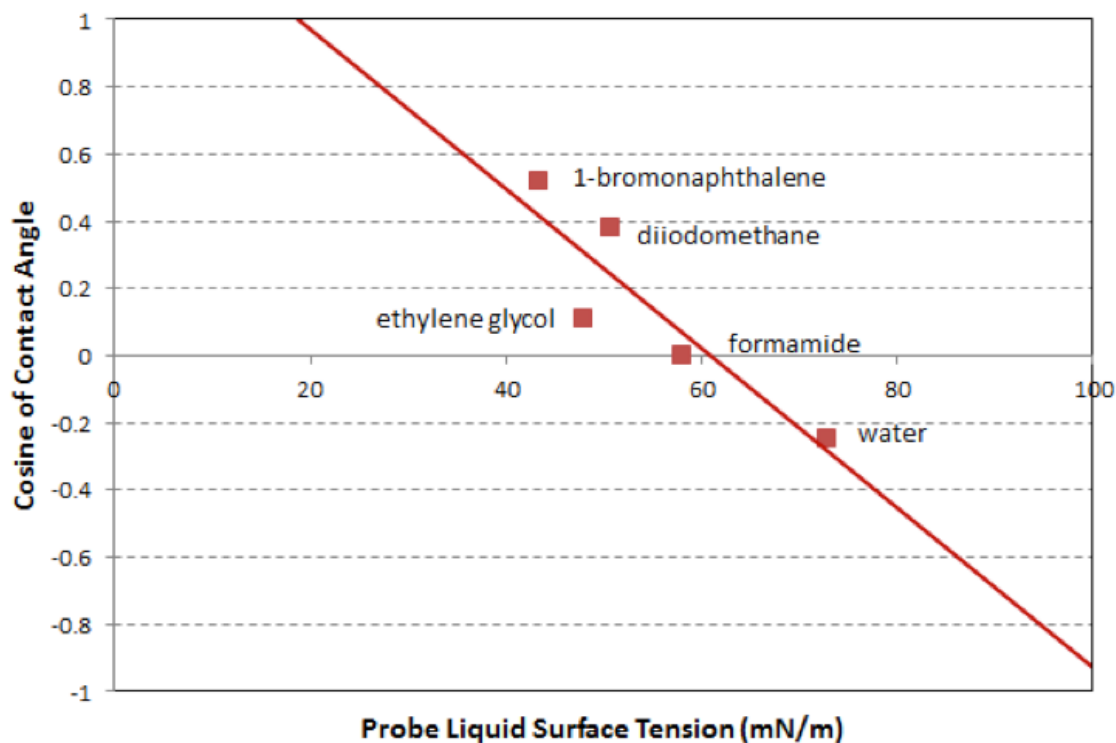


Figure 2. Zisman-Plot for one sample with five probe liquids.

Zisman's theory is the simplest theory on surface free energy; useful but with limitation. The theory is a one-component model and it treats the surface free energy as a whole. In recent years researchers have considered the critical surface tension as the dispersive component rather than the total surface free energy. In general, the Zisman theory works best for non-polar surfaces such as polyethylene and polypropylene. However, with a surface that has a polar component, such as polyimides, polyesters, glasses, ceramics and metals, Zisman theory becomes inadequate. In practice, Zisman method is not commonly applied, mainly due to insufficient theoretical justification and time-consuming investigation procedures. In order to make a Zisman-Plot, at least two different probe liquids are required for the tests; tests with five or more probe liquids are common.

The modern multiple-component surface free energy theories divide the surface energy into different components. These components are based on intermolecular forces, consisting of van der Waals forces, include orientation force, inductive force, dis-

persion force, and hydrogen bonding force. Various theories exist depending on how to interpret these forces involved in the surface interactions and how to calculate the average contributions of these acting forces. These energy analyses are based on Young-Dupré Equation on work of adhesion, W_{SL} . Young-Dupré Equation is a mathematical representation of the change of free energy of the liquid drop due to deformation equal to the free energy change due to adhesion of the liquid with the solid.

$$W_{SL} = \gamma_S + \gamma_L - \gamma_{SL} = \gamma_L \quad (2)$$

The Owens-Wendt theory is one of the surface free energy theories that contain two-components for surface free energy [3]. Owens-Wendt theory divides the surface free energy into one dispersive component and one polar component. The dispersive component accounts for van der Waals and other non-site specific interactions. The polar component accounts for hydrogen bond and dipole-dipole interactions. Equations (3) and (4) are mathematical descriptions of the Owens-Wendt theory.

$$\gamma = \gamma^d + \gamma^h$$

$$W_{SL} = 2(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^h \gamma_L^h}) \quad (3)$$

Where superscripts d and h are for dispersion and hydrogen component respectively; subscripts S and L are for solid and liquid respectively. The work of adhesion is the geometric mean of two component interaction.

Combining Equation (2) and (4), one can get Equation (5).

$$2(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^h \gamma_L^h}) = \gamma_L (1 + \cos \theta) \quad (4)$$

Using Equation (5) and 2 probe liquids with known surface tension components and their two measured contact angles one can solve the two simultaneous

equations to derive the two components and the total values for the solid surface free energy.

The Kaelble-Uy theory has a closed mathematical expression. It also assigns dispersion and polar components for the surface free energy. However, they do not include the contribution of the hydrogen bonding force. Equations (3) and (4) are rewritten as

$$\gamma = \gamma^d + \gamma^p \quad (6)$$

$$W_{SL} = 2(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p}) \quad (7)$$

Combining Equation (2) and (7), one can get Equation (8).

$$2(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p}) = \gamma_L (1 + \cos \theta) \quad (8)$$

(3) Wu theory is another two-component theory for surface free energy similar to Owens-Wendt theory. However, Wu theory applies approximation of harmonic mean instead of geometric mean for surface interactions. Equation (4) is rewritten as

$$W_{SL} = 4\left(\frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}\right) \quad (9)$$

Combining Equation (2) and (9), one can get Equation (10).

$$4\left(\frac{\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + \frac{\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}\right) = \gamma_L (1 + \cos \theta) \quad (10)$$

(5) Wu proposed that this equation should be used for high energy surfaces, such as mercury, glass, oxides and graphite, while the harmonic mean should also be good for the dispersive components in the cases of polymer surfaces [4].

The acid-base theory splits the surface free energy

into long-range interaction, Lifshitz-van der Waals (LW) component, and short-range interaction, Lewis acid-base (AB) components. This three-component model of surface free energy was proposed by van Oss and coworkers [5]. In acid-base theory, the work of adhesion is a function of the products of the LW, acidic and basic components of the solid and the liquid. The acid component characterizes the propensity of a surface to interact with liquids that have the ability to donate electrons. The base component characterizes the propensity of a surface to interact with liquids that have the ability to accept electrons. Equations (3) and (4) can be rewritten as

$$\gamma = \gamma^{LW} + \gamma^{AB} = \gamma^{LW} + 2\sqrt{\gamma^+ \gamma^-} \quad (11)$$

$$W_{SL} = 2(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}) \quad (12)$$

Combining Equation (2) and (12), one can get Equation (13)

$$2(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}) = \gamma_L (1 + \cos \theta) \quad (13)$$

Here, the work of adhesion caused by LW component can be expressed by the geometric mean. However, the work of adhesion caused by AB component cannot be expressed in the same way, as the basic components of the surface only interact with the acid components of the liquid, and vice versa.

The acid-base theory has two components specific for polar interactions, so it works best for surfaces that are capable of accepting or donating electrons such as inorganic surfaces, organometallic surfaces and surfaces containing ions. For example, it is widely used in the paper industry to characterize the paper surface whose surface properties could be acidic, neutral or alkaline. For applying the acid-base model, three probe liquids are required and at least

two liquids should have acid-base components. A protocol for determining the surface free energy of dental materials using the Acid-Base theory has provided a guide on how to select the probe liquids and how to process the data to obtain more meaningful results [6].

The Kitazaki-Hata theory is a three-component model that divides the surface free energy into dispersion, polar and hydrogen bond components. As with the acid-base theory, a geometric mean was used to account for the contributions of each energy component. Equations (3) and (4) are expressed as

$$\gamma = \gamma^d + \gamma^p + \gamma^h \quad (14)$$

$$W_{SL} = 2(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p} + \sqrt{\gamma_S^h \gamma_L^h}) \quad (15)$$

Combining Equation (2) and (15), one can get Equation (16)

$$2(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p} + \sqrt{\gamma_S^h \gamma_L^h}) = \gamma_L (1 + \cos \theta) \quad (16)$$

As a three-component model, the Kitazaki-Hata model requires three probe liquids in measurements.

It is interesting to note that because each theory has its own assumptions and limitations, there is not one theory that can be universally applicable to all solid surfaces and probe liquids. The common practice of surface energy analysis at present time relies on proper combination of probe liquids and theories in order to obtain a reasonable and meaningful surface free energy for a solid. In general, non-polar probe liquids work better for non-polar surfaces and polar liquids for polar surfaces. For non-polar surfaces, the theories that do not include specific molecular interactions (such as acid-base or hydrogen bond-

ing) are preferred. For polar surfaces that involve various molecular interactions, multiple-component theories are preferred so as to reveal such interactions. Sometimes a particular model will yield useful data and other times it will not owing to the change in combinations of the probe liquids and the test surfaces. Scientists and engineers may need to work with more than one theory in practice. One common misunderstanding for choosing the surface free energy theory is to think that the more components are in the theory, the more accurate the surface free energy measurement results are. In spite of all limits, surface free energy analysis through contact angle measurements still remains a popular choice for its component level analysis capability and ease of operation.

Contact Angle Measurement Techniques

Although the concept of surface free energy is complex and its measured value may depend on the combination of probe liquids and chosen theories, contact angle measurement itself is simple and straightforward. Contact angle is mostly measured using a camera-based goniometer by recording and analyzing the profile of a liquid droplet deposited on a surface. The contact angle profile data obtained may be analyzed through several fitting methods such as half-angle ($\theta/2$) method, tangent method, and curve fitting method. The $\theta/2$ method determines the half angle between the baseline and the apex point of the droplet. The tangent method emphasizes the droplet profiles near the two end points of the droplet. The curve fitting methods fit a droplet to the profile of a circle or an ellipse. Although a real droplet might be distorted slightly by gravity or surface features, it generally fits well to a circle profile. The analyses by circle fitting and $\theta/2$ method are preferred to the tangent method and ellipse fitting. The ellipse fitting and tangent method are more useful when advancing and receding angles are of interests or testing surfaces are not uniform. Figure 3 shows an automatic contact angle meter with a rotating base equipped at Ebatco's Nano Analytical and Testing Lab. This contact angle meter can measure static contact angle, contact angle as a function of time, advancing and receding angles,

and sliding angle. It can also be used to determine liquid surface tension through pendant drop technique, and most importantly, to perform surface free energy analysis using all of the above described theories.



Figure 3. An automatic contact angle meter with a rotating base.

Figure 4 shows a contact angle meter that can be used for surface free energy analysis of specimens with miniaturized dimensions. This contact angle meter is thus called Micro Contact Angle Meter. This micro contact angle meter is specially designed for the needs of measuring contact angle at the microscale, for instance, on microscopic patterns, thin filaments, wires, single fibers, hairs, catheters, stents, electronic circuit traces, etc. The shown micro contact angle meter mainly consists of a vertical camera mounted above the stage for pinpointing the microscopic features for analysis, a horizontally mounted camera for measuring contact angle, and a pneumatic capillary liquid dispensing system for making micron size droplets. Since evaporation or absorption into certain solid samples of microscopic droplets occurs rapidly, images must be continuously captured from the instant the droplet adheres to the surface. Therefore, a 60 frame per second capture speed is standardized on the instrument with higher speeds up to 100,000 fps optional.

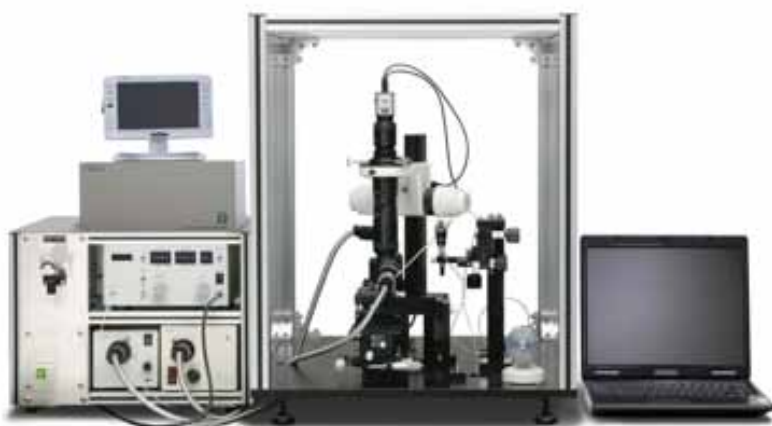


Figure 4. Left: The micro contact angle meter, Right: The top-view camera, horizontal measuring camera, capillary liquid dispenser and sample stage.

Applications of Surface Free Energy Analysis

Biomaterials

A biomaterial is defined as any substance (other than a drug) or combination of substances, synthetic or natural in origin, which can be used for any period of time, as a whole or as a part of a system which treats, augments, or replaces any tissue, organ, or function of the body. Biomaterials have constant contacts with biological systems such as blood or body fluids. A biomaterial's surface properties are critical to fulfilling its proper functions. The adherence of cells to a biomaterial and determining the biomaterial biocompatibility are closely related to the surface free energy of the biomaterial. Cells are attracted to the surface through van der Waal's forces and plurivalent cation bridging. A surface less attractive to cells requires a very low (preferably zero) blood-biomaterial interfacial tension [7]. The surface free energy of biomaterials and the work of adhesion can be used to predict cell adhesion to the material surfaces and hence to provide information on material blood compatibility.

Below is an example of surface free energy analysis for biomaterials performed in Ebatco's Nano Analytical and Testing Laboratory. Two types of gelatin samples were tested for surface free energy analysis. The gelatin is translucent solid, derived from collagen obtained from various animal by-products. Gelatin capsules are used in food and pharmaceutical industries as shells for holding drug and nutrient ingredients. The surface free energy analysis

of these gelatin capsules could help researchers to figure out how these capsules response to the water, why they tend to adhere to each other or how to avoid capsules adhering to the container surface after being stored. Two probe liquids: water, a polar liquid, and diiodomethane, a non-polar liquid, were selected for the surface free energy analysis of two kinds of gelatin samples. Table 1 shows the surface free energy components and total values of the two probe liquids according to the theories of Owens-Wendt, Kaelble-Uy and Wu. With the components of each liquid known for the desired theories, the surface free energy is calculated based on the measured contact angles each probe liquid formed with the gelatin samples.

Surface Free Energy Analysis of Solid Matters

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Table 1 Surface free energy components of two probe liquids

Theory of Energy Analysis	Owens-Wendt			Kaelble-Uy			Wu		
Probe Liquid	SFE (mJ/m ²)			SFE (mJ/m ²)			SFE (mJ/m ²)		
	d	h	Total	d	p	Total	d	p	Total
Water	21.8	51.0	72.8	21.8	51.0	72.8	22.1	50.7	72.8
Diiodomethane	49.5	1.3	50.8	48.5	2.3	50.8	44.1	6.7	50.8

*d = dispersion component, h = hydrogen-bond component, p = polar component

Table 2 Surface Free Energy Analysis of Two Gelatin Samples

Theory of Energy Analysis			Owens-Wendt			Kaelble-Uy			Wu		
Sample	C.A. (deg)		SFE (mJ/m²)			SFE (mJ/m²)			SFE (mJ/m²)		
	Water	Diiodomethane	d	h	Total	d	p	Total	d	p	Total
Gelatin 1	87.5	57.5	27.5	3.6	31.1	26.9	3.7	30.6	24.5	8.6	33.1
Gelatin 2	73.3	59.5	24.0	11.3	35.3	22.5	12.0	34.5	21.3	16.7	38.0

As can be seen from Table 1, the surface free energy components used by the three different theories vary although the total surface free energy is the same value for each probe liquid. This provides an example for the differences existing in the theories. It also suggests that it would be better to consider multiple theories when performing surface free energy analysis. Table 2 shows the surface free energy of two gelatin capsule specimens obtained based on the Owens-Wendt, Kaelble-Uy and Wu theories. Even though each theory calculated the surface free energy differently for each gelatin sample, their measurement results on each sample are not drastically different from each other. All theories have measured lower total surface free energy values for gelatin type 1 than type 2. The more significant difference existed in the surface energy components. Gelatin type 2 has higher contributions from polar/hydrogen bond components for its surface free energy, which means that it has more specific interactions with other surfaces.

Powders

Powdered materials widely exist in soils, clays, pigments, polymers, and pharmaceuticals. Powders can be formed naturally or through grinding. It is trickier to determine surface free energy of powder materials through conventional contact angle measurements. One approach is to measure contact angle after the powder is compressed into pellets. These pellets usually are rough and porous. In addition, the compression may cause plastic distortion of the topmost powder particles. All these factors could cause measurement errors in contact angle in comparison to working with smooth and flat surfaces of the same material.

Another approach is through micro contact angle analysis provided the individual powder particle is large enough. This approach can be done with individual powder particles in sizes larger than a few microns.

The most popular way to measure contact angle of fine powders is through the infiltration rate method based on capillary rising phenomenon. Instead of directly measuring the contact angle using a goniometer, the value is obtained by applying the Washburn equation. The infiltration rate method uses powders packed into a vertical column. When the base of the column contacts with a liquid, the liquid will infiltrate the void spaces between the powder particles. The contact angle of the particles is calculated based on the distance of liquid infiltration. According to Washburn equation, the rate of penetration, V , of liquid into small cylindrical capillaries could be expressed as:

$$V = \frac{R_{\text{eff}} \gamma_L \cos \theta}{4\eta l} \quad (17)$$

where R_{eff} is the effective interstitial pore radius of the bundle of capillaries, γ is the surface tension of the liquid, θ is the contact angle, η is the viscosity of the testing liquid, and l is the depth of liquid penetration [8].

The infiltration rate method does not require high-resolution cameras, nor does it need to take the shape of the individual powder into account. Since the measurement of the liquid infiltration distance is difficult, it is possible to use weight increase from the liquid infiltration when measuring the infiltration rate, given that the packed height of the powder is controlled. The infiltration rate method for powder contact angle measurement is normally carried out on a surface tensiometer.

Table 3 and Figure 5 present the contact angle measurement results for three kinds of grain flour samples. Under conventional circumstances, measuring the contact angle of flour with a contact angle meter or goniometer would prove difficult due to the size of flour powders. With the infiltration rate method, determining the contact angle becomes possible and relatively easy. After determining the capillary radius, the contact angle was calculated via the infiltration rate method for each flour sample. As seen in Table 3, the contact angles for the three kinds of flours are relatively similar despite differences in the capillary radius.

It is obvious that the infiltration rate method could be used for surface free energy analysis of powders since it can be used to measure powder contact

angles. The ability to determine surface energy of powders like flour is of beneficial for many industries including the food, biomedical, pharmaceutical and chemical industries.

Table 3 Flour Contact Angle Measurement Results

Flour Type	Capillary Radius (μm)	Contact Angle (deg)
Bread Flour	270.45	85.06
General Flour	295.84	86.09
Soy Flour	201.96	87.73

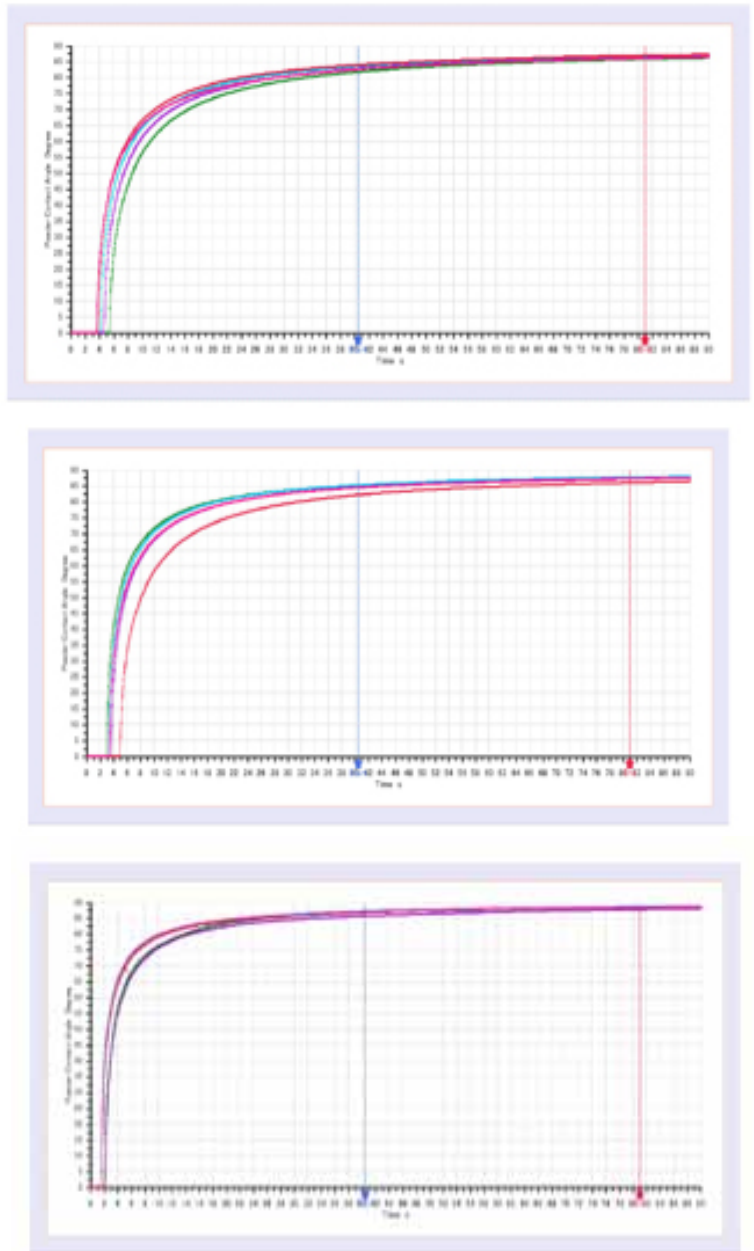


Figure 5. Powder contact angle test results for Bread Flour (top), General Flour (middle) and Soy Flour (bottom).

High Surface Free Energy Surfaces

For high surface energy solids, such as metals, ceramics and fresh minerals, most liquids would completely spread out on such surfaces to form a zero contact angle. The conventional methods for measuring surface free energy based on contact angle difference among various probe liquids are not possible in such cases. Schultz has developed a method of determining the surface free energy components for such surfaces [9]. The method was based on the measurement of the contact angle of water on such a solid when it was submerged into the second liquid medium. Usually, hydrocarbons like *n*-hexane, *n*-octane, *n*-decane, and *n*-hexadecane are used as the submerging liquids.

First, the dispersive component of the surface free energy was determined. According to the Young's Equation:

$$\gamma_{SL2} = \gamma_{L1L2} \cos \theta_{SL1} + \gamma_{SL1} \quad (18)$$

where γ_{SL2} , γ_{L1L2} , and γ_{SL1} are the interfacial free energies of S-L₂, L₁-L₂, and S-L₁ interfaces, respectively. θ_{SL1} is the contact angle of a droplet of liquid L₁ on solid S in liquid L₂.

According to Fowkes, γ_{SL2} and γ_{SL1} can be rewritten as

$$\gamma_{SL1} = \gamma_S + \gamma_{L1} - 2\sqrt{\gamma_S^d \gamma_{L1}^d} - I_{SL1}^p \quad \text{and} \quad (19)$$

$$\gamma_{SL2} = \gamma_S + \gamma_{L2} - 2\sqrt{\gamma_S^d \gamma_{L2}^d} - I_{SL2}^p$$

where γ and γ^d are the surface free energy and its London-dispersion force component, and I_{SL}^p is the non-dispersive interaction. Substituting Eqs (19) into Eq (18) yields

$$\gamma_{L1} - \gamma_{L2} + \gamma_{L1L2} \cos \theta_{SL1} = 2\sqrt{\gamma_S^d} [(\gamma_{L1}^d)^{1/2} - (\gamma_{L2}^d)^{1/2}] + (I_{SL1}^p - I_{SL2}^p) \quad (20)$$

In the case where Liquid L1 is water and Liquid L2 is *n*-alkane, the term, I_{SL2}^p may be neglected since the

surface free energy of *n*-alkane consists of only the London-dispersion energy. Therefore, Eq (20) can be rewritten as

$$\gamma_W - \gamma_H + \gamma_{WH} \cos \theta_{SW} = 2\sqrt{\gamma_S^d} [(\gamma_W^d)^{1/2} - (\gamma_H^d)^{1/2}] + I_{SW}^p \quad (21)$$

The plot of $(\gamma_W - \gamma_H + \gamma_{WH} \cos \theta_{SW})$ against $[(\gamma_W^d)^{1/2} - (\gamma_H^d)^{1/2}]$, shown in Fig. 6, should give a straight line with intercept I_{SW}^p and slope $2(\gamma_S^d)^{1/2}$. Once the γ_S^d and I_{SW}^p are available, the polar component of the surface free energy was found to be a linear function of the square root of the polar term of the surface free energy of liquids. The I_{SW}^p can be calculated as

$$I_{SW}^p = 2(\gamma_S^p \gamma_W^p)^{1/2} \quad (22)$$

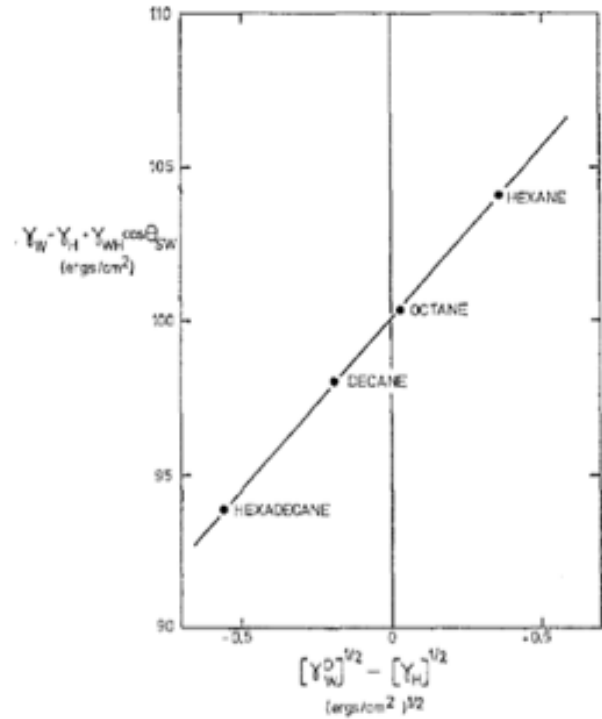


Figure 6. Plot of $[\gamma_W - \gamma_H + \gamma_{WH} \cos \theta_{SW}]$ against $[(\gamma_W^d)^{1/2} - (\gamma_H^d)^{1/2}]$ [9].

Muscovite mica was studied as a model high surface energy solid in Schultz's work. The dispersive component of mica surface was 30 mJ/m² and the polar component of mica surface was 90 mJ/m². The total surface free energy of mica was 120 mJ/m².

This result was exactly the same as the surface free energy determined by cleavage of non-matching mica sheets.

Concluding Remarks

Concepts, theories, techniques and applications of surface free energy analysis for solid matters are presented in this paper. Several popular theories based on Young-Dupré adhesion theory and contact angle measurement approach were discussed. An example application of surface free energy analysis was given on gelatin samples. Surface free energy analysis for difficult powder samples and high surface energy samples are also introduced. We hope this brief introduction and overview paper will assist scientists and engineers to better understand and grasp these promising and useful techniques for surface free energy analysis of solid matters.

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see page 3

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Calendar

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