SYMPOSIUM N
Polymer Gels for Emerging Technologies
March 29 - 31, 2005

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* Invited paper
Here we describe a highly crosslinked hyperbranched polymer that rapidly swells and shrinks in dichloromethane solvent in response to the addition of acid or base. The polymer was based on 1,2,3-triazoles units conveniently synthesized under mild conditions in aqueous-organic solvent mixtures using Cu(I) catalyzed [3+2] cycloaddition of azides and alkynes with triazole forming triazines. The insoluble polymer swelled rapidly in trifluoroacetic acid-containing AM *N1.5 and showed significant interaction of the polymer with the solvent. The swelling properties and penetrant diffusivities were determined using binary mixtures of solvents. The solvent transition temperature decrease with increased concentration, and (3) peaks in temperature increase. The gel transition temperature is near the LCST 8:30 AM *N1.1 Directed Motion and Cargo Transport through Propagation of Polymer Gel Volume Phase Transitions. Ulrich Wiesner1, Lilib Yehgaziarian2, Surbhi Mahajan1, Claude Cohen3 and Carlos D. Montemagn04; 1Materiins Science & Engineering, Cornell University, Ithaca, New York; 2Biological Engineering, UCLA, Los Angeles, California; 3Chemical & Biomolecular Engineering, Cornell University, Ithaca, New York.

One of the fundamental problems in biotechnology is the transformation of energy into directed motion and transport on very small scales. Hybrid devices driven by molecular motors have been engineered but are often limited through required specific environmental conditions. Here we demonstrate a prototype controlled synthetic soft machine built from a thermosensitive polymer hydrogel for which motion is based on a mechanism different from those employed in earlier gel-based devices. The moving gel is capable of transporting cargo and can be stopped and restarted at any time. We generale the directional movement of cylinder-type hydrogels by spatially controlled propagation of the volume phase transition along their length, demonstrating velocities of about 15 micrometers per second for cylinder diameters of the order of 0.1 millimeter. Since gel volume changes are diffusion controlled, miniaturization to the micron scale can be expected to dramatically enhance gel speeds beyond what is currently observed in small scale devices. We anticipate that this principle will be widely utilized in a variety of areas in biotechnology including microfluidics, robotics and drug delivery.

We discuss the gelation, phase-separation, and calorimetric properties of copolymers composed of N-isopropylacrylamide (NIP) and maleic (MAc) or acrylic acid (AAC). These copolymers exhibit a lower critical solution temperature (LCST) as well as a liquid to gel transition. In these polymers both gelation and phase separation occur on temperature increase. The gel transition temperature is near the human physiological temperature. This property makes these polymers useful in drug-delivery systems. The transition temperature depends on the degree of copolymerization, the pH of the environment, and the polymer concentration. We present a simple theoretical model to describe the properties of these and related families of LCST gel-forming polymers. The central assumption of the model is that the properties of the system are determined by the release of water molecules associated with the polymers at low temperatures. We assume that the water release is a local phenomenon in which the monomers act non-cooperatively. Experimental results for NIP-Mac and NIP-AAC copolymers, and results derived from the model exhibit several common features of both gelation and phase separation temperatures with concentration, (2) a gelation temperature decreases with increased concentration, and (3) peaks in the specific heat associated with both gelation and phase separation.


Active materials are non-equilibrium systems where energy is constantly injected. These are the basis of many biological systems such as the actin-myosin gels but also vibrated sand piles or even bird flocks. The cell cytoskeleton is mostly composed of actin filaments interacting with myosin motors. It is active in the sense that energy is consumed; the energy is provided by the hydrolysis of AdenosineTriPhosphate. We generalize here the Maxwell visco-elastic model to describe the actin-myosin complex. We explicitly take into account the active motors and an anisotropic reaction of the actin filaments. Following the lines of the classical Martin Parodi Pershan hydrodynamic theory of nematic liquid crystals, we write Onsager relations between generalizad forces and fluxes and the active Onsager coefficients associated to the myosin molecular motors. We then give examples of applications of this theory to problems inspired by cell motility. We discuss the formation of a lamellipodium at the leading edge of advancing cells and present an oversimplified model of the motion of fish keratocyte skin cells.
to the increase in LCST due to hydrolysis of the ester bond in the butyrolactone ring. Properties of the copolymer were characterized by DSC, HPSEC, and 1H NMR. The copolymers were synthesized in a three-step process involving the reaction of hydroxyl groups in an alcohol (butanol) with butyrolactone to form a hydrophobic block, and then reaction with an amine to form a hydrophilic block. The resulting copolymers exhibited a lower critical solution temperature (LCST) of 30.6°C, which is significantly lower than that of the corresponding homopolymers.

The LCST of the copolymers decreased with increasing butyrolactone content, as shown in the figure. This decrease in LCST is attributed to the increased hydrophilicity of the hydroxyl groups in the hydrophilic block. The LCST was also found to increase over time, indicating some degree of hydrolysis during storage.

The incoherent scattering function for hydrogen in the copolymers was found to be 93% of the total incoherent scattering. This indicates that hydrogen is the dominant incoherent scatterer in these materials, and the incoherent scattering cross section was used to infer the molecular dynamics of the polymer chain. The results showed that the incoherent scattering cross section was influenced by the hydrophobic interactions in the butyrolactone ring, which hindered the collapse of the copolymers.

The incoherent scattering cross section of other atoms such as carbon was also measured, and the results showed that carbon also contributed to the incoherent scattering. This indicates that the incoherent scattering is not just due to hydrogen, but also to other elements in the copolymer.

The results of this study suggest that the incoherent scattering cross section can be used to infer the molecular dynamics of polymer chains, and that the copolymers exhibit a lower LCST than the homopolymers. This could have implications for the design of new materials with tunable hydrophilic-hydrophobic properties.
The use of low-valent metal complexes for the polymerization of alpha- amino acid-N-carboxyanhydrides (NCAs) will be presented. Using these initiators, we have prepared block copolypeptides containing a variety of both hydrophilic and hydrophobic domains. The hydrophilic chains are composed of either cationic or anionic residues and the hydrophobic chains are composed of natural non-polar residues or synthetic hydrophobic units such as phenylalanine. We have focused our efforts on the self-assembly of block copolypeptides in solution, primarily employing water as the solvent. By working with polypeptides, we expected that the secondary/tertiary structure of the material would substantially alter the structures of the polymers. The controlled aggregation of block copolypeptides into discrete ordered structures would yield materials valuable for biomedical and materials applications.

Examples include use of polypeptide gels as well as growth of the complex would favor selective interactions with different biological surfaces. The properties of hydrogel-forming amphiphilic block copolypeptides will be discussed.

2:30 PM *N2.4
Enzymatically Crosslinked Hydrogels: The Role of Polymer Composition in Gelation and Adhesion at the Biomaterial/Interface. Bi-Huang Hu, Marshi Ritter Jones, Roger Warren Sands and Philip Messersmith; Biomedical Engineering Department, Northwestern University, Evanston, Illinois.

With increasing frequency, polymer hydrogels intended for wound repair and tissue engineering are being designed with the capability of in-situ gelation from a liquid precursor, allowing minimally invasive administration via syringe and needle. The catalytic activity of biologically relevant enzymes in polymeric hydrogels under physiologic conditions without the need for polymerization initiators, monomers and other potentially harmful compounds necessary for gel formation by other methods. In this talk I will briefly describe our efforts to utilize the enzyme transglutaminase, to induce rapid gelation of polymer-peptide conjugates. The use of combinatorial methods leading to optimization of the polymer composition for rapid gelation will be described. Due to the ability of the enzyme to crosslink peptide-polymer conjugates to extracellular matrix proteins of connective tissues, an added benefit of this approach lies in the potential enhancement of adhesion between the biomaterial and adjacent native tissues. Preliminary results demonstrating coupling between hydrogel components and tissue interfaces will be presented.

3:30 PM *N2.5
Environmentally Responsive Hydrogels with Tunable Rigidity Constructed via Peptide Folding and Consequent Self-Assembly. Darrin J. Pochan; Materials Science and Engineering, University of Delaware, Newark, Delaware.

By using peptide molecules in the materials self-assembly design process, one can take advantage of inherent biomolecular attributes, intramolecular folding events and self-assembly to more traditional self-assembling molecular attributes such as amphiphility, to define hierarchical material structure and consequent properties. Importantly, intramolecular folding events impart a molecular-scale mechanism for environmental responsiveness at the material level (e.g. infinite change in viscosity of a solution to a gel with changes in pH, ionic strength, temperature). Design strategies based on small (less than 24 amino acids) beta-hairpin peptides will be discussed. The self-assembly construction process is predicated on the peptides first intramolecularly folding into the beta-hairpin conformation from a random coil conformation. Importantly, the scaffold assembly is completely reversible with pH or temperature by reversibly folding and unfolding the constituent peptides that, in turn, assemble or disassemble the scaffold, respectively. In addition, the rigidity of the gel scaffold can be tuned via the magnitude of the environmental stimuli, e.g. gels triggered with temperature and pH maintain their structure at higher temperatures due to faster folding and self-assembly kinetics. Local hydrogel structure, both fibrillar struts and crosslink points, can be altered by changing peptide length. Finally, the hydrogel networks are also mechanically responsive in that they can quickly reheat into a rigid material after shear thinning due to the self-assembled nature of the underlying network. The molecular design and self-assembly principles, including a model to explain the inherent tunability of the final gel networks that underlie the observed morphological and rheological material, will be presented. Laser scanning confocal microscopy, cory transission electron microscopy, oscillatory rheology, small-angle and ultrasmall-angle neutron scattering, spectroscopy, and cytotoxicity results will be presented.

4:00 PM N2.6
Surface-Patterned Hydrogels with Controlled Bioactivity. Peter Kirsch, Our Lady's Spies and Matthew Libera; Stevens Institute of Technology, Hoboken, New Jersey.

We are interested in controlling the spatial distribution of proteins on surfaces across cellular and subcellular length scales using patterned hydrogels. To do this, we have been using a focused electron beam in a field-emission scanning electron microscope (SEM) to radiation crosslink water-soluble polymers such as polyethylene glycol (PEG) and poly(carboxylic acids). We have exploited the inherent tunability of the final gel networks that underlie the observed properties. The resulting hydrogels on silicon or glass surfaces with nanoscale and microscale feature sizes. Using hydroxy-terminated PEG we have achieved to create gels with swell ratios between unity and fifteen depending on the degree of radiation crosslinking, adhesion properties can be modeled using the Flory-Rehner formulation modified for one-dimensional swelling. To increase the flexibility of creating high-swelling PEG gels which resist non-specific protein adsorption but to which specific proteins can be covalently bound. We use bovine serum albumin (BSA) to amplify the number of amine groups, and we further demonstrate that different proteins can be covalently bond to different hydrogel pads on the same substrate to create multifunctional surfaces. Finally, with the aim of making a three-dimensional hydrogel-based device, we have explored the interaction of focused electron beams with bulk hydrogels previously synthesized by conventional UV crosslinking methods, and we show that the local properties can again be modulated at cellular and sub-cellular length scales.

4:15 PM N2.7
Liquid Crystal Gels Self-Assembled From Block Copolymers. Neal Scruggs, Rafael Verdugo and Julia Kornfield; Chemical Engineering, California Institute of Technology, Pasadena, California.

Block copolymers with long side-group liquid-crystalline (LC) midblocks and LC-phobic end-blocks form a physical network that swells readily in a small molecule LC to form nematic gels. Using ultralong (>800 kg/mol) side-group liquid crystal polymers (SGLCP) for the midblock enables gelation at relatively high polymer concentration (~5-8% polymer). The materials provide model systems in which the molecular weight between crosslinks is well defined and determined by the length of the polymer midblock. Similar to LC elastomers, an initially unaligned, polydomain gel aligns under applied strain, creating a monodomain that is oriented well enough to generate clear conoscopic figures. Furthermore, a novel stripe pattern attributed to semi-soft elasticity forms when the gels are subjected to electric fields or when the order parameter of the LC solvent changes. When an electric field is applied to the gels the switch-on time is somewhat slower than that of the pure LC solvent but the polymer network exhibits a restoring force in fast restitution force once the field is removed.

4:30 PM N2.8
Enzymatic Cross-linking of Short Synthetic Peptides and Peptide-polymer Conjugates to Cartilage. Matthew Elizabeth Ritter Jones and Philip Messersmith; Biomedical Engineering Department, Northwestern University, Chicago, Illinois.

Hydrogels have been explored as matrices for cartilage regeneration, however the lack of adhesion of hydrogels to native cartilage is a major obstacle to their application. Tissue transglutaminase (Tg) is a member of the transglutaminase family of enzymes that catalyze the cross-linking reaction between lysine and glutamine residues of proteins. Tissue transglutaminase is found in cartilage and is considered to be one of the enzymes used to form permanent cross-links between matrix extracellular matrix (ECM) components, such as osteonectin, osteopontin, collagen II and fibronectin. Some researchers have demonstrated that Tg can be used to create cartilage-cartilage bonds, and small synthetic Tg substrate molecules such as monomalic acid have been found to couple to collagen II. Our lab has synthesized short Tg substrate peptides, Ac-FKG and Ac-GQQQLG, and has...
used these peptides to modify polyethylene glycol (PEG) polymers and cross-link them into a hydrogel. Hypothesizing that interfacial adhesion between hydrogels and other tissue engineering constructs and native tissue will be important in successful repair or regeneration of cartilage, the current study sought to determine if these peptides have the capability to react with ECM components of cartilage. We examined the ability of these peptide-modified polymers, to react with intact pieces of cartilage in the presence of tTG. Digested cartilage and commercially available ECM components of cartilage were reacted with these peptides in the presence of tTG and Western blot analysis used to determine which cartilage ECM proteins had reacted with the peptides. Our results demonstrate that these peptides are coupled to cartilage ECM components by tTG, suggesting the possibility that better integration of peptide based hydrogels with native cartilage is possible through enzymatic cross-linking to native tissue.

4:45 PM N9.9

There has been a considerable interest on bio-hydrogel adhesives that can solidify in situ and form strong and durable bonds. In this study a Poly(methyl methacrylate)-poly(tert-butyl methacrylate)-poly(methyl methacrylate) (PMMA-PtBMA-PMMA) triblock copolymer was synthesized via anionic polymerization. The midblock was then converted to methacyric acid (MAA), and L-3,4-dihydroxyphenylalanine (DOPA) was attached to the MAA midblock. The adhesive properties of DOPA containing hydrogel were studied via an axisymmetric adhesion test. A rigid flat punch coated with Titanium (Ti) was brought into contact with flat hydrogel surface. The work of adhesion and the energy separation was measured by breaking the interfacial bonds formed when the surfaces were in contact.

SESSION N3: Poster Session: Polymer Gels Tuesday, March 29, 2005
8:00 PM Salons 8-15 (Marriott)

N3.1

In recent years there has been a growing appreciation for the need to avoid calcium-based phosphate binders in patients with chronic kidney disease so as to prevent the long-term complications of accelerated vascular disease. The paucity of available medications has led to the overwhelming use of the nonabsorbable synthetic polymer, polyallylamine (sevelamer HCl, Renagel®, Genzyme Corp., Cambridge, MA). It is a highly effective binder due to the anionic charge of protonated amine groups, removing phosphate in vitro at approximately 3 meq (288 mg) drug. Rigorous pharmacokinetics studies also involve the synthesis of novel polymer systems for forming threedimensional networks using conventional rheological techniques. Recent advances in instrumented indentation techniques (IIT) have provided the capability to measure the mechanical and physical properties of polymers over much smaller length scales than are accessible through conventional rheometry. In this work we use a commercial instrumented indentation system to investigate the viscoelastic deformation properties of two model physical gels. The first model system was an undrained gelatin, a model biopolymer that forms aqueous polymeric gels through a time dependent association of single helices into physical crosslinking sites. Ordinance gelatin is the material of choice for evaluating the damage inflicted by ballistic events on the human body. The second model system was a synthetic gel composed of a styrene-isoprene-styrene triblock copolymer dissolved in a midblock selective solvent where the polystyrene end blocks aggregate to form physical crosslinking sites. This triblock copolymer is readily available as the precursor to pressure sensitive adhesive formulations. In this work we compare the viscoelastic deformation properties of these model gels to standard ordnance gelatin gels using several different radii flat punch indenters. The small strain frequency dependent moduli over a range of frequencies (10-200 Hz) along with stress relaxation experiments were used to investigate differences in the stress dependent deformation behavior of the two different gel systems. Our goals in characterizing these systems are two-fold: 1) develop a methodology to reliably characterize a soft gel (E = 1 MPA) with IIT and 2) demonstrate the advantages of the model synthetic physical gel relative to a standard ordnance gel. For example, ordnance gelatin is calibrated with a test shot before use as a target. This calibration provides a qualitative approach to understanding the relationship between inflicted damage and the gelatin structure and mechanical properties, which can vary due to the nature of ordnance gelatin.
better understanding of the stress dependant deformation behavior of the test gel before testing will ultimately provide more quantitative information in an elastic event after test is completed. The physical gels are a route to achieving the required understanding of the deformation behavior.

N3.4 Structures of Hydrophilic Polymer-Silica-Phosphoric Acid Composites and Applications in Intermediate Temperature Fuel Cells. Wenbin Han¹, Ken Tasaki² and Galen Stucky¹,²,³
¹Mitsubishi Research and Innovation Center, Yokohama, Japan; ²Department of Chemistry and Biochemistry and Materials Department, University of California, Santa Barbara, California; ³Department of Mechanical Engineering and Materials Science, University of Southern California, Los Angeles, California.

Organic-inorganic hybrid hydrogel-polymer-silica hybrids doped with proton conducting acid H₃PO₄ were prepared using a sol-gel process. Polymer-xH₃PO₄-ySiO₂ composites were obtained for y<0.8 and y<20%, where x was the molar ratio of PO₄³⁻ with polymer repeat unit and y was the weight percentage of SiO₂ in the composite. TGA data showed that the composites were thermally stable up to 200°C. The glass transition temperature of the composites dropped from 178°C to 46°C when y was changed from 0 to 6.9. Thin film FTIR and ¹H, ²³Si and ³¹P NMR studies revealed that in addition to the hydrogen bonding between the hydrophilic groups of the polymer and the phosphoric acid, the silanol groups reacted with the PO₄³⁻ groups as well, which suggested a semi-IPN structure of the composites. The proton conductivity of the composites increased with acid content and relative humidity (R.H.). At high acid content (x>3), the composites had higher conductivity than Nafton at 50°C and 100% R.H., and comparable conductivity to Nafton at high R.H. (>60%). Therefore, the composites have potential applications in intermediate temperature fuel cells.

N3.5 Ion Transport in Decoupled Hybrid Organic-Inorganic Polyelectrolyte, Flavio Leandro de Souza, Edson Roberto Leite and Roberto Longo; Materials Science and Engineering, UFSCar, Sao Carlos, Sao Paulo, Brazil.

In this work we described the chemical synthesis strategy to obtain helical free chain hydrogel formation of a single-phase hybrid organic-inorganic polymer electrolytes leading to a good Li ion conductivity at room temperature (~10⁻⁵ (ohm·cm⁻¹)), the hybrid polymer studied here is prepared, by a sol-gel non-hydrolytic process, with citric acid, tetracetyl orthosilicate and ethylene glycol, forming polymer chains. It is well that the ion transport above Tg (glass transition temperature), in typical polymer electrolyte, is strongly coupled to segmental motions of the polymer chain, resulting in a VTF ionic conduction behavior (after Vogel-Tamman-Fušcher). The hybrid organic-inorganic polymer obtained from this strategy showed a Tg of ~70°C and an Arrenius behavior regarding temperature dependent ionic conductivity for temperatures higher than Tg was obtained. Such remarkable behavior characterizes a segmental motion decoupled polymer. This hybrid organic-inorganic polymer electrolyte (polyelectrolyte) showed activation energy of 0.23 eV, indicating a fast ion transport mechanism. Such characteristics indicate a fast ion transport mechanism in a segmental motion decoupled behavior is reported for a hybrid polyelectrolyte. For the best of our knowledge, this is the first time that a segmental motion decoupled feature is reported for a hybrid organic-inorganic polyelectrolytes.

N3.6 Properties of Galactose-Derivatized Thermosensitive Hydrogels and Their Uses in Culture of Hepatocytes. Jyh-Ping Chen¹ and Shiu-Chung Cheng¹; ¹Graduate Institute of Biochemical and Biomedical Engineering, Chang Gung University, Taoyuan, Taiwan; ²Department of Chemical and Materials Engineering, Chang Gung University, Taoyuan, Taiwan.

In this study we examined the behavior of freshly isolated rat hepatocytes cultivated within thermo-sensitive hydrogels containing the monomer N-isopropylacrylamide (NIPAAm). Based on the difference in molecular structure created by the presence or absence of a cross-linker during polymerization, the hydrogels can be divided into two groups, a thermo-sensitive injectable hydrogel (cross-linked) and a thermo-sensitive polymer hydrogel (not cross-linked). These novel three-dimensional scaffolds mimic the in vivo extracellular matrix for hepatic tissue engineering. Loosely cross-linked polymer(NIPAAm-co-acrylic acid) [P[NIPAAm-co-AAc]] thermo-sensitive injectable hydrogels were synthesized with M,N-metacryloyl) as a cross-linker in buffer solutions. Thermo-sensitive polymer hydrogel was synthesized by copolymerizing NIPAAm and AAc in benzene with AIBN as an initiator. Galactose residues were introduced into the hydrogels by modifying the AAc groups with galactosylated derivatives (galactosylamin) or by co-polymerizing with galactose-containing co-monomer (allyl galactopyranoside). By introducing galactose into the hydrogels, cell adhesion and metabolic functions are expected to be substantially improved by inducing specific interactions between hepatocytes having a galactose-specific receptor, and the polymer molecules. The hydrogels were characterized by NMR for chemical structures, GPC for molecular weights, UV-VIS for drug release, and FTIR for the complex solution temperature, SEM for pore sizes and structures, dynamic rheometry for viscoelastic properties, and resorcinol sulfuric acid assay for galactose content. Freshly harvested rat hepatocytes were seeded into the hydrogels by injection into the hydrogel or by mixing with the polymer hydrogel. Hepatocytes could maintain their viability up to a month with MTT assays and Laser Scanning Confocal Microscopy by a LIVE/DEAD fluorescence assay. Phase-contrast microscopy, HE and Alcian Blue stains and TEM were used to evaluate the morphology, distribution of extracellular matrix, and ultrastructure of hepatocytes aggregates. Metabolic functions of cells were confirmed by secretion of albumin and urea-N during the culture period for up to 3 weeks. These results indicate that thermosensitive hydrogels can serve as a useful tool for studying cell-material interactions within 3-D structures and have the potential to be used as ideal scaffolds for hepatic tissue engineering applications.

N3.7 Characterization of H+Nafion®/Alcohol Gels. Steven Romel Givens, Christian Pellerin, John Rabolt and Bruce Chase; Material Science and Engineering, University of Delaware, Newark, Delaware.

Thermoreversible gels were formed by dissolving DuPont H Nafion® perfluorosulfonic acid in several alcohols, including 2-propanol, 2-butanol, 2-pentanol, and 2-octanol. These gels show a reversible liquid/solid transition with each of these alcohols. The gel behavior was not seen in H+Nafion®/alcohol systems using the primary alcohol isomers. The short-range molecular structure of the thermoreversible H+Nafion®/alcohol gels was investigated using FTIR, absorption and ATR techniques, and Near-IR FT Raman scattering. Using previously characterized spectra of polytetrafluoroethylene (1) as a means of identifying the vibrations of the helical zigzag CP2 backbone of H+Nafion®, particular attention was given to interpreting the interaction of the pendant sulfonic acid group with the solvent. Hyper differential scanning calorimetry was used to determine the gel thermal properties and transition point as well as the enthalpies of these transitions. (1) Rabolt and Frasconi Macromolecules Vol 11 No.4 pp.740-745 1978


Resorcinol Formaldehyde (R/F) foam aerogels have been used in the fabrication of shell targets for Inertial Fusion Confinement experiments at the University of Rochester. Recent cryogenic experiments with R/F shells have necessitated a larger size R/F foam than the standard R/F formulation. The R/F foams are synthesized by the polycondensation of resorcinol with formaldehyde in a slightly basic solution. A method for controlling the pore size of R/F foams has been investigated. It involves increasing the catalyst concentration in the polymerization process leading to reaction and diffusion limited aggregation which in turn leads to changes in the pore size distribution of the foam. Foams with varying pore size distribution have been made using this technique. These foams have been characterized using a variety of techniques including SEM, nitrogen adsorption porosimetry, and visible light scattering. Results of our study are presented in the following section.

N3.9 Sliding Friction of Gel under a High Load. Jian Ping Gou and Takayuki Kurokawa; Graduate School of Science, Hokkaido University, Sapporo, Japan.

Industrial or environmental problems caused by high frictional surfaces of materials always exist in our daily life. Looking for materials with a low surface friction has been one of the classical and everlasting research topics for material scientists and engineers. Studies on the surface sliding friction of water swollen hydrogels on solid surfaces as well as between gels reveal the richness and complexity of gel friction.[1] [2] Hydrogels exhibit a wide range of frictional coefficients from an order of 10⁻³ to 100 in magnitude, depending on the interfacial interaction between the polymer network and the opposing substrate. It is also elucidated that polymer brushes on solid surfaces can drastically reduce the surface friction coefficient to a value as low as 10⁻⁴ if the polymer brush has a
repulsive interaction with the sliding substrate. [3] The low friction of gel should have enabled the gel to find a wide application in many fields where low friction is required. Unfortunately, conventional hydrogels, especially polyelectrolyte gels that show a failure stress less than 0.1MPa, are mechanically too weak to be practically used in any stress or strain bearing applications. This is for well understood that the force required for breaking bonds between cross links for the network of polymer chains is too low. The mechanical weakness has hindered not only the extensive application of hydrogels as an industrial and biomedical materials, but also the further development of hydrogels research under high pressure (> MPa). Recently, we discovered a general method to obtain strong hydrogels by inducing a double-network (DN) structure for various combinations of hydrophilic polymers. [4] The DN hydrogels, containing 60-65% water, exhibit fracture strength of a few to several tens of MPa. This makes it possible, for the first time, to study the gel friction under a pressure range as high as 1-10 MPa, over which utility is required. In this study, we report the friction of high strength DN gel against glass under a load up to 2.5 MPa order. The friction of the gels swollen with different viscous solutions is investigated over a wide velocity range. A velocity-viscosity conversion relationship is established, which indicates that the motion of the polymer chain plays an important role on the gel friction. From the velocity-viscosity conversion relationship, a master curve that is characteristic to the adsorption-hydrodynamic lubrication transition is obtained, which indicates that the adsorption model proposed by our previous work[2] still valid even under a load up to 2.5 MPa order. References [1] J. P. Gong, Y. Iwasaki, et al., J. Phys. Chem. B.1999, 103, 6001. [2] J. P. Gong and Y. Osada, J. Chem. Phys. 1998, 106, 8062. [3] J. P. Gong, T. Kurokawa, et al., J. Am. Chem. Soc. 2004, 123, 5582. [4] J. P. Gong, Y. Katsuyma, T. Kurokawa, Y. Osada, Adv. Mater. 2003, 15, 1155.

N3.10

The Volume Phase Transitions of Acrylic Acid/KAoline Powder Superabsorbent Composite. Jiuhua Wu and Jianming Liu, Huaqiao University, Institute of Materials Physical Chemistry, Quanzhou, Fujian, China.

Superabsorbent possess the better volume phase transition properties, which have aroused widely interest in many applications. It was observed first by Tanaka in 1978, because it is possible to apply in molecular biology, drug delivery, self-healing composites and bioMEMS. A novel superabsorbent, sodium acrylate/kaolinite powder composite was synthesized by using partly neutralized acrylamide as monomer, N,N'-dimethylacrylamide as crosslinker, and 2,2-dimethoxy-2-phenyl acetophenone as initiator. The UV initiator, 2,2-dinethoxy-2-phenyl acetophenone, exhibits a high reaction rate and is obtained within 1-2 minutes. The gelation time of the UV polymerization is shortened compared to classical gelation times in the range of 30-120 minutes. A series of these PVA-VA scaffolds were investigated, it was found that the volume phase transition of superabsorbent decreases with the increase of the ionic strength of exterior solution. The different anions do not affect the volume phase transition of the composite. The volume phase transitions depend on the pH value of solution, the volume phase transitions of the composite is the largest (800) when the pH value of the system equal to 7. The volume phase transitions of superabsorbent depend on the crosslinking density and the functional group on the superabsorbent. The group of the superabsorbent can be controlled by adjusting the neutralization degree of acrylic acid monomer during the preparation of materials, and the volume phase transitions of the composite can be realized suitable. This work was supported jointly by the National Natural Science Foundation of China (No. 50773004) and the Provincial Science and Technology of Fujian, China (No. 2004HZ01-3, No. 2002H02).

N3.11


Gels are crosslinked polymeric networks that swell in organic solvents. Although much work has been done in this field [1], the role that entangled chains play in fully polymerized gels and how these entanglements affect the gel's physical properties has not yet been fully understood. In this work, we investigate the influence of solvent present during UV polymerization of poly(tert-butyl acrylate) [poly(t-BA)] gels. The gels are comprised of the monomer tert-butyl acrylate (t-BA), ethylene glycol dimethacrylate (EGDMA) crosslinker, and a UV initiator 2,2-dimethoxy-2-phenyl acetophenone (DMPA). Three different solvents were introduced to this monomer solution in increasing weight percent of the total solution, spanning 0 to 20 wt%. The samples showed different mechanical properties with t-BA and thus allow us to probe how solution during polymerization influences physical properties such as modulus and degree of swelling. The effects of total solvent content on various material properties was also investigated. Swelling studies were performed in solvents whose solubility parameter ranged from 15.1 to 47.9 MPa^1/2. Solvent swelling experiments indicate that the swelling ratio increases with wt% of solvent present during polymerization. Rheological testing indicates a corresponding increase in modulus with wt% of solvent. The results of equilibrium swelling experiments are compared to theoretical calculations and rheological data in order to estimate the solubility parameter and molecular weight between crosslinks for the gels. [1] K. Sivasailam and C. Cohen, J. Rheol. 44 (4), 897-915 (2000).

N3.12

Mechanical Properties in Large Deformations of Hydrogels. Reberle Wehrle, Guillaumin Le Douarin, Dominique Houret and Costantino Creton; ESPCI, Paris, France.

Although the mechanical properties of polymer gels have been well studied, most of these studies focus on the linear viscoelastic properties. However, gels often show a very poor resistance to fracture which is closely connected with the large strain deformation properties of the gel. Although empirical knowledge on how to increase the gel hardness is available, we will present some results on the deformation properties of gels in the large strain regime and on their fracture properties.

SESSION N4: Biomedical Applications of Hydrogels

Chair: Phil Messersmith

Abstract Withdrawn

8:45 AM N4.1


Tissue engineering aims to create functional tissue using cells seeded onto 3-D scaffolds, providing an alternative to traditional therapies. Tissue engineering can encompass diverse technologies such as growing patches of living tissue in vitro to regenerative therapies to re-growing healthy tissue in situ. Despite the wide differences between approaches, they share one common need: a scaffolding material with properties mimicking natural tissue. The work described here investigates a new group of synthetic organic materials for use as tissue engineered scaffolds, poly(vinyl alcohol) (PVA)–amino acid (AA) hydrogel foams. Previously our lab reported a unique interaction between PVA and AA monomers during the production of novel hydrogels [1]. We have previously shown that by combining PVA-AA hydrogels with colloidal gas aphrons (CGA) techniques we can create foams containing uniform bubbles with diameters on a micrometer scale [2]. The size scale of these CGAs or microfoams makes them a favorable choice for tissue scaffolds, where pores between 100 and 200um are desired [3]. We have characterized and fabricated a series of these PVA-AA scaffolds to examine the effects of polymer Mw, amino acid identity and incorporation of collagen I on final material properties. The largest property differences were seen with changes in polymer Mw and the introduction of collagen I. Volumetric swelling ratio (Q) increased with decreasing Mw. Degree of crosslinking, calculated from volumetric swelling ratio and Flory's equation [4], was found to be unaffected by polymer Mw however crosslinking decreased upon the introduction of collagen I. SEM imaging of the scaffolds found pores ranging in size from 50–300um (PEI Siron 30, 3KV beam). Degree of interconnectivity appears to increase with the introduction of lower Mw polymer, and preliminary permeability studies support this claim. In addition mechanical testing of the scaffolds tensile properties and a study of hydrolytic degradation of the scaffolds at 37°C are in progress. This work was supported by National Institute of Health grant R24HL64387, NSF-Engineering Research Center grant EEC-5929161 and an American Heart Association Pre-doctoral fellowship. 1. Nair P., et al. Bioresorbable Porous Polymers Containing Amino Acid Networks as Scaffolds for Tissue Engineering. Society for Biomaterials Transactions, 2001. 2. Donaldon E., et al. Novel Tissue Scaffolding Materials Based on Poly(vinyl alcohol) and Amino Acid Hydrogels. in 7th World Biomaterials Congress, 2004. Sydney, Australia. 3. Jockenhoevel S., et al. Fibrin gel - advantages of a new scaffold in cardiovascular tissue engineering. European Journal of Cardio-thoracic Surgery, 2001. 19:424-430. 4. Flory P.J. Principles of Polymer
Hydrogels provide a unique, largely aqueous environment for 3D cell culture, and when locally modified with appropriate signaling molecules, these scaffolds can mimic the function of extracellular matrix molecules. While the gel environment is often >90% water, the microscopically structured chemistry and architecture play an important role in dictating cell morphologies, degradation and erosion, and the secretion and distribution of extracellular matrix molecules. In this work, hydrogels were synthesized to present local signals to human mesenchymal stem cells (hMSCs) that induce osteogenesis, maintain cell function and enhance matrix mineralization. A significant amount of research has focused on the differentiation of hMSCs in monolayer culture, very little is known about their differentiation potential when cultured in a three-dimensional environment. In particular, results will demonstrate approaches to modify the structure and chemistry of hydrogel hMSC carriers to facilitate osteogenic differentiation and bone formation. First, the macroscopic hydrogel properties including water content, mesh size, and degradation rate were tuned to support 3D hMSC culture. Second, the composition of the extracellular hydrogel environment was varied and methods were developed to locally present osteogenic factors (e.g., dexamethasone) to induce hMSC differentiation. Third, the gel architecture was tailored and mineralization occurred. Specifically, sequences that correspond to known signaling domains in ECM functions important for tissue growth and healing. Significant interest has also been demonstrated via intracellular and cellular assays that the inclusion of hydrophobic N-alkyl acrylamide blocks into hydrogels can be attained via interpolymer complexation of the gel. The importance of using temporal controls in the network structure for tissue engineering applications is demonstrated through degradation-controlled proliferation of differentiating hMSCs. Single and multi photon imaging was used as a non-invasive technique to explore living cell behavior, especially differentiation of hMSCs, as a function of the local gel chemistry and delivery of osteogenic factors.

Polyacrylamide-derivatized polymers for the noncovalent assembly of Bioactive Hydrogels. Nori Yamaguchi1,2, Le Zhang1, Eric M. Furst2 and Kristi L. Kiick1,2. Department of Materials Science and Engineering, University of Delaware, Newark, Delaware; 2Delaware Biotechnology Institute, Newark, Delaware; 3Department of Chemical Engineering, University of Delaware, Newark, Delaware.

Protein-polyacrylamide interactions play important roles in a myriad of physiological and pathological processes. Materials in which assembly, mechanical response, and biological properties are controlled by these interactions may therefore be responsive to the biological environment and find use in a variety of biomedical applications. Despite this potential utility, polyacrylamide-peptide interactions have only recently been demonstrated as useful in the assembly of noncovalently associated networks. We report here the production of a heparin-modified, poly(ethylene glycol) star copolymer that can be used in the assembly of bioactive hydrogel networks via multiple strategies and that is also competent for the delivery of biological growth factors. The noncovalent assembly of hydrogels can be attained via interaction of the heparin-modified polymer with a variety of heparin-binding proteins and peptides. The rheological properties of the hydrogels have been measured via optical probe micro rheology and bulk rheology methods and can be controlled by the specific peptide-saccharide interactions. The release of therapeutically important proteins from these heparinized hydrogels has also been studied via in vitro, in vivo, and cellular assays and is correlated with the erosion of the network. The ability to manipulate the properties of the hydrogels will provide novel materials for use in controlled drug delivery and other biomedical applications.

Di(ethylene glycol) acrylamide block copolymers for on-chip protein adsorption and DNA purification. Karl William Putz1,2, Thomas K. Chieal1, Meena Babu1, Chung-Yan Koh2, Xihua Lu2 and Annelise Barlow1. 1Chemical and Biological Engineering, Northwestern University, Evanston, Illinois; 2Chemistry, Northwestern University, Evanston, Illinois. A series of di(ethylene glycol) acrylamide block copolymer nanogels were fabricated for use as a sieving matrices that adsorb proteins and lipids and allow DNA to pass through in microchip electrophoresis. Large-scale-chip technologies will be a powerful tool due to their small sample volume, ease of use, small physical size, and rapid analysis, in such settings as biowarfare agent determination and third-world disease detection. While several DNA sensing technologies have pushed the limit of species resolution, it has been necessary to devise new methods to purify DNA "on chip". Previous experiments have demonstrated that the inclusion of hydrophobic N-alkyl acrylamide blocks into linear polyacrylamide polymer matrices altering macromolecular flexibility during electrophoresis due to interactions between the copolymer and hydrophobic amino acids. Highly charged and hydrophilic DNA molecules were not only allowed to pass through the copolymer, but also separated based on their length. The current series of di(ethylene glycol) acrylamide-acrylamide block copolymers and crosslinking the polymer chains using divinylsulfone. The hydrodynamic content was verified by 1H NMR and the size of the nanogels was determined by dynamic light scattering.

Temperature-responsive Culture Surfaces. Masayuki Yamato, Institute of Advanced Biomedical Engineering and Science, Tokyo Women's Medical University, Tokyo, Japan.

The possibility of re-creating various tissues and organs for the purpose of regenerative medicine has received much interest. However, the field of tissue engineering has been restricted by the limitations of conventional approaches. A main factor is control for traditional scaffold-based technologies is cell sheet engineering, which utilizes temperature-responsive culture dishes. On these surfaces, ultra-thin hydrogel layer is created by the covalent grafting of the temperature-responsive polymer, poly(N-isopropylacrylamide), by electron beam irradiation. This temperature-responsive layer is around 20 nm in thickness, and allows for the non-invasive harvest of cultured cells as intact sheets by simple temperature reduction. Since this cell sheet harvest doesn't require proteolytic treatment, cell-cell junctions, other membrane proteins and the deposited extracellular matrix all remain intact. Therefore, harvested cell sheets readily adhere and integrate with other cell sheets and tissues. Current research progress in the field of cell sheet engineering for the reconstruction of various tissues including cornea, periodontal ligaments, cardiac tissues, urinary bladder, liver, and esophagus will be shown. In addition, the early clinical outcome will be also provided. We believe that cell sheet engineering, which employs temperature-responsive intelligent surfaces, will overcome the problems that have limited conventional approaches and establish a new basis for regenerative medicine.

Colocalization of RGD and PHSRN Epitopes on PEG Surfaces Influences Osteoblast Function. Daniele S. W. Bengt1 and Kristi L. Kiick1,2. 1Chemical and Biological Engineering, University of Colorado, Boulder, Colorado; 2Howard Hughes Medical Institute, Chevy Chase, Maryland.

Poly(ethylene glycol)-based hydrogels provide many ideal characteristics for cell delivery and tissue regeneration; however, synthetic platforms often require modification to present cells with ECM cues that actively and selectively stimulate desired cellular functions important for tissue growth and healing. Significant interest has emerged in the design of cell scaffolds that incorporate peptide sequences that correspond to known signaling domains in ECM proteins and study how this influences cell attachment and subsequent cellular functions. The cell-adhesive domains of fibronectin have been well studied, and an Arg-Gly-Asp (RGD) sequence is a critical site. Since its identification as a pessive cell-adhesive peptide, RGD has been widely investigated in terms of biomaterial modifications. More recently, a Pro-His-Ser-Arg-Asp (PHSRN) sequence, although not biologically active, was found to enhance the cell-adhesive activity of RGD. In this work, we synthesized macromolecular PEG nonomers with pendant RGD functionalities, RGD and PHSRN spaced by a 13-mer of glycine that mimics the spacing of these epitopes in fibronectin (RGDG13PHSRN), and a scrambled peptide sequence of...
These monomers were copolymerized with divinyl PEG macromers to produce hydrogels used to provide a controlled environment. Cells were seeded on these surfaces to determine the effects, if any, of the synergetic epitope sequence on cell attachment and function. Cells incorporating RGDG13PHSRN increased osteoblast adhesion and spreading, viability of the solution gradually increases as the sol becomes interconnected to form a rigid three-dimensional, porous structure - the gel. Materials with tailor made porosity, morphology, and chemical functionality are particularly important in the development of highly directed biological networks. Three-dimensional porous gel scaffolds are created using polymer sol gel chemistry and fundamental optical lithography. These three dimensional matrices are then used to map the morphological growth changes both optically and electrically. Sol gel has the same chemical make-up as glass - silicon dioxide. Unlike glass, though, sol gel is porous and can be made at low temperatures. This property is used to optically visualize encapsulated neural networks. The cells are stabilized in the matrix, but retain and exhibit their natural properties. These three dimensional biological neural network matrices would be suitable platforms for understanding neuron proliferation and understanding cell-cell communication in in-vitro environments.


Human embryonic stem cells (hESCs) are being studied as a possible source of cells for the treatment for many diseases (e.g. diabetes, Parkinson’s, leukemia). However, it is difficult to control the maintenance of hESCs, since conditions for self-renewal are not completely understood. As such, hESCs are typically grown on a feeder layer of mouse cells (i.e., irradiated but viable cells) and are considered xenografts and cannot be used clinically. Control of hESCs growth and differentiation on a synthetic three-dimensional matrix are key steps in the development of hESC culture conditions. If hESCs can be derived and maintained on a synthetic hydrogel system, then it may be possible to eliminate pathogen transmission associated with mouse or human feeder layers. Also, the hydrogel system can increase the reproducibility of culture conditions and elucidate the requirements for hESC maintenance. In this study, hESCs were grown on a hydrogel consisting of loosely crosslinked poly(N-isopropylacrylamide-co-acrylic acid) (p(NIPAAm-co-AAc)). The p(NIPAAm-co-AAc) was crosslinked with an acrylated peptide, poly(acrylic acid-graft-RGD) to provide cell binding domains, during the polymerization of p(NIPAAm-co-AAc). An important feature of this hydrogel is that the gel stiffness is tunable by varying the concentration of: (a) the crosslinker, and (b) the linear p(AAc)-g-RGD chains. The hydrogel undergoes a lower critical solution temperature (LCST) at ~35 °C. Rheological measurements were performed over a frequency range of 0.001 Hz - 10 Hz to determine the complexity (G’) and loss angle (tan δ). The sample G’ of p(NIPAAm-co-AAc) at 22 °C at 1 Hz was 72.4 Pa ± 2.3 (SE), and at 37 °C at 1 Hz was 129.1 Pa ± 6.1 (SE). The hydrogel was polymerized in 12-well plates and sterilized by the use of ethanol. hESCs were cultured on the hydrogel surface and optimal hESC culture conditions were used. 2 hESCs were evaluated by immunofluorescence against the Oct-4 transcription factor, a highly specific and necessary hESC marker. Initial results indicate the ability to solidify in-situ, a property that facilitates their use as adhesional forming materials for drug delivery and tissue repair. In this paper, we describe the use of stimuli responsive liposomes to induce rapid thermal gelation of DOPA-modified polymers. Liposomes containing entrapped sodium periodate were mixed with DOPA-modified polymers to create a viscous liquid capable stable during storage at room temperature. Warming of the liposome/polymer mixture to body temperature induced release of periodate from liposomes and rapid crosslinking of polymer into a hydrogel. Finally, we report the preliminary results of tissue adhesion experiments in which the shear strength of porcine skin tissue slices adhered by in-situ formation of hydrogel between tissue surfaces was determined.
Dynamic 

Hydrogel Micro and Nano-Environments as Functional Units in Biomedical Fabrication. John Jongchan Bang\textsuperscript{1,2},  

Kurina Arcaute\textsuperscript{1,2}, Richard Adams\textsuperscript{3,4}, Luis Ochoa\textsuperscript{1,2} and Ryan Blaine Wicker\textsuperscript{1,2}.  

\textsuperscript{1}Mechanical and Industrial Engineering, University of Texas at El Paso, El Paso, Texas; \textsuperscript{2}W. M. Keck Biomedical Manufacturing and Engineering Lab, El Paso, Texas.

Polymers have received extensive examination for use in tissue engineering. However, cytocompatibility remains a critical issue in their application. As part of a continuing feasibility study for using stereolithography (SL) layered manufacturing to develop precise implantable PEG hydrogel constructs, cytocompatibility of NIH/3T3 cells with photopolymerized PEG hydrogels at different concentrations of two photoinitiators was investigated. SL has been used extensively in industrial applications and its benefits are beginning to be recognized by the tissue engineering community. In particular, by way of layered manufacturing and optical-based reaction kinetics, SL affords the opportunity for fabricating PEG hydrogel constructs with precisely located bioactive agents for use in guided angiogenesis, nerve regeneration, and other applications. NIH/3T3 cells were seeded on photocured PEG hydrogels in 24-well dishes with different concentrations of Irgacure 2959 and HMPP for two experimental conditions: one design tested the effect of different photoinitiator concentrations on cell survival and the other tested the osmolarity effects of PEG hydrogels on cell survival. The photocuring process was conducted in a cell culture lab with a portable UV source. The PEG monomer solution containing photoinitiators was filtered before use. For each design, seeded cells on 24-well dishes were examined for their morphologic changes and growth patterns. Four relevant observations were made for future SL applications in PEG hydrogel production. First, the intrinsic cytocompatible characteristics of the photoinitiators could be influenced by concentration adjustment. For example, low concentration of HMPP allowed compatible levels of cell survival without compromising optimal physical properties of the hydrogels. Second, the level of hydrogels used for cell growth seems to influence cell growth pattern on the hydrogels. Third, osmolarity seems to influence cell growth behavior. A dramatic difference in cell growth pattern was observed between 24-hour DMEM pretreated hydrogels and non-treated ones. Fourth, physical properties, such as temperature, can be tailored and controlled in photopolymerizing hydrogels. These findings suggest that hydrogels can be tailored to control cell growth in a wide range of applications.
different surfaces narrowed in the experiment using DMEM pretreated PEG hydrogels. Further evaluations on the variables investigated in this preliminary study with various types of cells are warranted so that the information can be utilized in a variety of SL PEG hydrogel construct fabrication applications so that the gels can be precisely tailored for the application.

The first enzyme, tyrosinase, catalyzes reactions between gelatin and chitosan yield a transient gel network with thermally-responsive properties (gelatin confers thermal-responsiveness). Tyrosinase-catalyzed reactions with the globular green fluorescent protein (GFP) yield a GFP-chitosan conjugate that can be spatially-localized in response to applied electrical signals (chitosan confers this responsiveness). The second enzyme, transglutaminase, catalyzes reactions between lysine and glutamine residues, and when this reaction is performed with gelatin, a covalently crosslinked hydrogel network is generated. This enzymatic crosslinking reaction occurs under mild conditions, and is being explored for in situ cell entrapment, and as a soft tissue adhesive. These results indicate that the potential of biological materials for fabricating self-assembling capabilities - biological materials often offer stimuli-responsive properties and they can be acted upon by highly selective biological catalysts.

Surface-attached polymer networks offer a powerful route towards soft surfaces with well-defined mechanical, physical and biochemical properties. Polymer networks not only provide a 3-dimensional scaffold capable of hosting a wide-array of functionalities, ranging from proteins to inorganic nanoparticles, but they can also undergo substantial swelling and contraction in response to specific stimuli, making them excellent candidates for "smart" surfaces with sensing and actuating characteristics. We introduce a facile method for fabricating hydrogel multilayers from photo-cross-linkable copolymers that can be crosslinked of hydrophobic, hydrophilic, or charged nature. The strategy involves integrating the photoactive monomer methacryloxybenzophenone (MaBP) along a polymer backbone, which is capable of forming covalent cross-links with aliphatic groups upon exposure to UV radiation at 365 nm. The approach is general in nature and facilitates the rapid fabrication of cross-linked multilayers through sequential deposition/irradiation steps with few restrictions as to the types of polymers that can be incorporated. In order to understand the swelling properties of such films, we have studied their swelling behavior with multiple-angle null ellipsometry in an ATR configuration, an analytical technique that yields information about the thickness and refractive index profile of the swollen layers. Ellipsometric measurements reveal that the volume fraction profiles of the swollen surface-attached networks can be controlled by the MaBP content; however, attachment of the network to a surface effectively constrains swelling to approximately the square-root of the unconfined state. In order to characterize and verify these layers, these films were fabricated by sequential bilayers of different types of networks were fabricated and verified with ellipsometry. Upon swelling, a discontinuous change in the volume fraction of the film could be found where the two layers were joined.

Inorganic-Inorganic Hybrid Surfaces by In-situ Self-Assembly for Controlled Drug Delivery - Detecting Pores by Positron Annihilation Lifetime Spectroscopy. Hubert Koller 1, Ansgar Boegh Petersen 1, and Anita Hild 1; 1 Institute of Physical Chemistry, University of Muenster, Muenster, Germany; 2CSIRO Manufacturing & Infrastructure Technology, Clayton South MDC, Victoria, Australia.

The oral application of drugs often requires encapsulation of the active component into a matrix that releases it with a controlled kinetic protocol. The first goal of this study was to explore the drug release kinetics for inorganic-organic hybrid gel matrices which are self-assembled in the incorporated drug molecule. The second topic was the characterization of pore space which is responsible for storage and delivery capacity. Diprydamol (Persantin) is a drug that is used for expanding the coronary vessel system. It was incorporated in situ into silica hybrid gels which are synthesized from tetraethyloxsilicate (TEOS), and a second molecular precursor, R-Si(OEt)3. By variation of the organic component in the drug carrier system, the interaction between host and guest was tailored to optimize the release behavior. The preliminary results indicate that the release kinetics: the hydrophobicity of the organic group, the sol-gel transition, pH value, and the presence of organic functional groups which produce hydrogen-bond capabilities or aromatic moieties into the matrix. The introduction of organic side groups in the matrix (phenyl, benzyl groups) leads to a very stable interaction between these groups and Persantin which has an aromatic core and aminealkyl side groups. A higher release was observed for alkyl groups (methyl, propyl) in the sol-gel matrix. Aromatic as well as alky groups increase the retarding properties of such drug carrier systems. On the other hand, acetoxypropyl side chains lead to a faster release, when these functional groups are increased in concentration. The single-precursor gel (TEOS), and most hybrid gels show an increasing microporous specific surface area after the dissolution experiment. Surprisingly, the materials with acetoxypropyl side chains show no increase in specific surface area after drug release, even though these gels have released the highest amount of Persantin. Therefore, we used positron annihilation lifetime spectroscopy (PALS) as an alternative means to study the porosity of the gels. Positrons can penetrate matter and localize in pores without the need for pore accessibility from the external surface. Positrons have a reduced lifetime due to pick-off annihilation with electrons from the surrounding environment. The lifetime depends on the size of the porosity suited to detect pores (within a few nm developing upon drug release, independent of whether or not the pores are directly connected to the external surface. With this tool, it was possible to clearly detect the evolution of pores depending on release time. It is concluded that acetoxypropyl groups block the pores for nitrogen adsorption. PALS is a very useful method to characterize the porosity of such biologically relevant surface internal structures.

The ability to form polymeric liquid crystalline assemblies coupled with a relatively low depolymerization temperature (<100 oC) make polysucyanates excellent candidates for preparing thin films with functionalized, anisotropic porosity. In this study, we have prepared poly(3-triethoxysilylpropyl isocyanate) by a cyanide initiated anionic polymerization to provide a rigid-rod polymer that can be sol-gel polymerized into highly crosslinked matrices. A variety of tert-butyl side groups were attempted in the preparation of liquid crystalline films with reagents (acid, base, and/or tetraethylorthosilicate and bis(triethoxysilyl)methane) introduced to introduce crosslinking of the polymer sidechains. These films were liquid crystalline, but cracked upon drying with and without the addition of drying control additives such as DMF. Biphasic formulations made crack-free, monolithic films from suspending a dilute organic solution of polysucyanate in toluene or xylene on top of an aqueous solution of acetic acid, water, and additives (ethylene glycol, triethylene glycol, or glycerol). The IR, porosity, solid state NMR, birefringence, SEM, and TGA were used to assess the morphology, surface area, and chemical functionality of the sol-gel films.
8:30 AM  **N6.1**


In a general sense, all gels can be viewed as comprised of a network, which gives the solid character, and a liquid phase which dilutes the network and controls also the dissipative properties. In between rubbers, where the network is essentially undiluted and classical polymer gels where the polymer fraction typically varies between a few percent and 20%, exists an intermediate category of materials where the polymer fraction is of the order of 50%, which are widely used as so-called hydrogels. Although the dynamic properties of these materials have been extensively investigated, the material characterization has been mostly limited to the linear viscoelastic properties. Yet, their non-linear elastic and viscoelastic properties play an important role. An important aspect of these concentrated gels is the role played by entanglements both in the nonlinear elastic properties and in the viscous dissipative properties. We will present some new results and interpretations for entangled systems based on styrene-isoprene copolymers, and on unentangled systems based on methymethacrylate-2ethyl-hexyl acrylate copolymers.

8:45 AM  **N6.2**

Abstract Withdrawn

9:00 AM  **N6.3**

Tough Hydrogels with Double Network Structure, Jian Ping Gong, Y. Kurokawa, R. Kuwahara, Y. H. Na, Y. Tanaka, and Y. Osada; 1Graduate School of Science, Hokkaido University, Sapporo, Japan; 2Creative Research Initiative "Sousei", Hokkaido University, Sapporo, Japan.

Hydrogels are composed of three-dimensional hydrophilic polymer network in which a large amount of water is interposed. Due to their unique properties, a wide range of medical, pharmaceutical, and prosthetic applications have been proposed. However, most of them are suffered from the lack in mechanical toughness, and only very limited applications have been realized. Recently, we have overcome the problem by discovering a general method to obtain high strength gels. The high strength gels are synthesized by a sequential two-step reaction. The first is rigid polyelectrolyte as the first network and flexible neutral polymer as the second one: 2) the first network is highly cross-linked, and the second is slightly cross-linked or even without cross-linking. The combination of hydrogel with the two networks, and the molar ratio of the two polymers are crucial in improving the resistance against stress. The optimized conditions are as follows: 1) Rigid polyelectrolyte as the first network and flexible neutral polymer as the second one; 2) the first network is highly cross-linked, and the second is slightly cross-linked or even without cross-linking; 3) the molar ratio of the second network to the first one is in a range several to a few decades. The dynamic light scattering (DLS) analysis of the DN gels shows a slow mode besides the gel mode (fast mode) for the DN gels with a loosely cross-linked 2nd network, which correlates with the increase in the strength of DN gels. The dynamics of slow mode cannot be explained in terms of reptational motion of the second component in the first network but is similar to the translational motion of the 2nd polymers in a semi-dilute solution. As the highly cross-linked first network has a high Young's modulus but is quite brittle on its own, we consider that large voids of first network may exist and the loosely cross-linked second network, exist in voids act as molecular crack-stopper by dissipating the fracture energy, preventing the crack from growing to a macroscopic level. [2] References [1] Gong, J. P.; Katsuyama, Y.; Tsukeshiba, H.; Gong, J. P.; Osada, Y.; Otake, S.; Kando, T.; Shibuya, M. Macromolecules 2004, 37(14), 5379.

9:30 AM  **N6.4**

Physical Properties of Interpenetrating Polymer Networks Formed by Grafting to Oxide Surfaces: Surface Characterization, Protein Adsorption, and Cell Detachment Studies, Lin, Fu-Chin Chuang, Wei-Chun Lin,3, Lin,3,Kueono, B.; 1Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois.

A contact mechanics methodology utilizing the quartz crystal microbalance (QCM) has been applied to study the spreading behavior of polymer solutions and gels. Changes in the series resonant frequency and in the dissipation are monitored as these materials are brought into contact with the electrode surface of the QCM. The technique is especially useful in studies of elastic polymer gels, where the elastic spreading over the surface of the QCM is limited by the elasticity of the gel. Simultaneous measurement of the applied loads and displacements, along with measurement of the QCM/gel contact area, the frequency shift, and the dissipation, enable us to calibrate the QCM as a contact sensor. While the frequency shift and dissipation both depend linearly on the contact area, measurements of the dissipation provide a more reliable indicator. The relationship between the dissipation and the contact area is determined by the solvent viscosity, and by the high frequency intrinsic viscosity of the system of interest. This result is consistent with previous results on the high frequency rheological behavior of polymer solutions.

10:30 AM  **N6.5**


When a saturated gel immersed in the same liquid is suddenly brought into contact with a smooth rigid indenter, the load required for the initial penetration is determined by the elastic properties of the gel, and the gel fluid, which act as an incompliant material. This gives rise to a pressure gradient in the liquid phase and the liquid flows until the pressure in it goes to zero everywhere, and all the stresses are transferred to the elastic network. As a result of the flow, the force needed to maintain a constant contact area relaxes with time. In this work, we study the feasibility of using an indentation test to measure of this time dependent force and to determine the elastic modulus, the Poisson ratio and the cooperative diffusion coefficient, D, of the network. Specifically, we...
consider a two-dimensional Hertz contact problem of a rigid circular cylinder indenting on a half space consisting of an elastic gel. The network of the gel is assumed to be linearly elastic and isotropic and liquid flow within the gel is assumed to obey Darcy law, which states that the flux is proportional to the pressure gradient. Exact expressions are obtained for the initial and final force required to maintain a given contact length. These expressions allow us to determine the elastic constants of the network. The permeability of the network can be obtained from the time dependent relaxation of the applied load. The relation between the applied load and the pore pressure is obtained by using a finite element method to obtain the pore pressure. Our finite element results show that for short times, load relaxation is a linear function of the square root of the time divided by a, where t is time and a is the contact width made by the circular indenter.

11:00 AM N6.7 Transport Properties of Polymer Gels, Wei-Chun Lin,1 Kenneth R. Shull,2 Ching-Yuan Hsu,3 Yi You Lin2 and Fu-Chin Chuang2; 1Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois; 2Department of Theoretical and Applied Mechanics, Cornell University, Ithaca, New York; 3Department of Civil Engineering, National Cheng Kung University, Tainan, Taiwan.

When a saturated polymer gel comes in contact with an indenter during an adhesion test, a common assumption made is that the solvent flow out of the polymer network is negligible. However, this assumption is not always valid: Under such deformation, solvent flow in a gel occurs as a result of the pressure gradient that forms when the indenter comes in contact with the gel. The local pressure of the gel is not equal to the osmotic pressure of its environment, and as a result the polymer gel is strained as solvent is squeezed out. An analysis of the kinetics of such a system leads to a novel method, which determines the permeability and elastic constants of a gel. To determine these transport and mechanical properties of a gel experimentally, a flat punch indentation method is used to study the behavior of poly(n-isopropylacrylamide) (PNIPAM) hydrogels in phosphate buffer saline solution at temperatures below and above the lower critical solution temperature (LCST) of 32°C. Stress-relaxation and oscillatory experiments are used to probe the response of the gel over different time scales.

11:15 AM N6.8 Structure and Mechanical Properties of Gelatin - Clay and Gelatin - Oxide Nanocomposite Gels in Bulk and Thin Film Form. Margarita Darder1, Anabel Ruiz-Hitzky1, Patrick Amarellis2, Eduardo Ruiz-Hitzky3, Andre Dubault4 and Henri Van Damme5; 1ICMM, CSIC, Madrid, Spain; 2CPMD, ESPCI, Paris.

Gelatin - a denatured form of collagen - forms non toxic biocompatible thermoreversible gels in water. Unfortunately for structural applications, the gel temperature is relatively close to room temperature and the mechanical properties are rather poor. The purpose of our study was to explore the possibility of increasing both the gel formation temperature and the gel mechanical properties by building and entangled biconfocal organic-inorganic network. Nanocomposite gels were prepared by mixing clays or oxide nanoparticles with gelatin. Nanoparticles with either lamellar (montmorillonite and sepiolite clay; perovskite oxides) or fibrous (sepiolite clay; vanadium oxide) morphology were used. The dispersion state of the mineral component in the aqueous organic phase was monitored by X-ray diffraction and transmission electron microscopy. The mechanical properties of the gel were investigated by conventional dynamical rheological measurements in stress-imposed shear strain conditions. The results show that large (lateral size) lamellar particles of nanometer thickness are extremely effective for increasing the gel formation temperature and the mechanical properties of the gel. Thin (a few tens of micrometers) self-supporting and well transparent films are easily obtained by water evaporation. Surprisingly, fibrous particles are much less effective, even at concentrations higher than the intercalation and exfoliation thresholds. The mechanical properties of the organic-inorganic films will be compared with those of pure clay films. The organic-inorganic mixed nanocomposite gels are attractive materials for conservation of antique wall paintings.

11:30 AM N6.9 Adhesion between Polymeric Fluids using a Probe Method. Regis Schach and Costantino Creton; Laboratoire PPMID UMR 7615, CNRS/ESPCI, Paris, France.

Relatively few studies have been carried out on the adhesion between polymeric fluids, and the problem remains poorly understood. However, this problem is critical for industrial applications. For example, in the tire industry the cohesion of the different layers of a tire before the final crosslinking process is directly related to the polymer-polymer adhesion of uncrosslinked elastomers, which are polymeric fluids. A key experimental obstacle for the understanding of this problem is the separation of the surface and the bulk contributions to adhesion for such liquid materials. The probe tack experiment, used in the Pressure-Sensitive-Adhesive (PSA) industry, is a powerful analytical tool capable of evaluating adhesion and cohesion of adhesives against rigid surfaces [1]. In this test, a flat steel probe approaches the adhesive layer (which has been deposited on a glass slide) at a constant velocity, applies a controlled compressive force during a set contact time and is removed at a constant debonding velocity while a CCD camera allows the observation of the debonding mechanism. This technique cannot be directly applied to the study of self adhesion of elastomers because the adhesion between the two polymers is greater than between the polymer and the substrate causing the debonding to occur between the substrate and the elastomer. To avoid this problem, we use chemical grafting of mercaptolines to chemically bond the polymer to the substrates: a silicon wafer grafted with a 1 μm polymer layer is glued on the probe and the second polymer layer (100 μm) is grafted to the glass slide. This modification of the probe tack experiment allows us to study the cohesive strength of elastomers. We present here results on the self adhesion of SBR Rubbers. We used three SBR rubbers with the same microstructure (20% styrene, 42% vinyl, 19% cis and 19% trans) but with different molecular weights (80 000, 160 000 and 240 000 g/mol). We observed different debonding mechanisms depending on the time of contact, the debonding velocity and the polymer used. For short times of contact, fast debonding rates and hard polymers we observed an interfacial crack propagation, though for longer contact times, cavitation occurs in the polymer. For very slow debonding rates and with soft polymers, we observed a liquid-like mechanism of debonding. We found that these different behaviours are directly related to the bulk rheology of the polymer, especially its retraction time, which sets the limit between elastomeric and liquid-like behaviour as well as the interdiffusion time at the interface. Finally, we propose a map of the mechanism independent of the molecular mass of the polymers, using two reduced parameters, the ratio of contact time to retraction time and the Deborah number. [1] Creton, C. MRS Bulletin 2003, 28, 434-439.

11:45 AM N6.10 Electric Field Effect on Adhesion of Poly(N-isopropylacrylamide) Gel. Victor Barinov, Robert Dabrowski and Kalle Leven; Chemical and Biological Sciences and Engineering, Polytechnic University, Brooklyn, New York.

Development of dispersive adhesive gels and physical-separation methods could have a major impact on technologies requiring reversible adhesion properties. The effect of applied electric field on the adhesion of poly(N-isopropylacrylamide) (PNIPA) hydrogel to aluminum was studied. PNIPA hydrogel was prepared by UV-induced polymerization. A pull-off adhesion test was employed to characterize the adhesion of a hydrogel sample to an aluminum dolly. Hydrogel was placed between two flat faces of aluminum dolly. By activating the load source, tensile load was increased within the system. When the load on the aluminum dolly reaches the critical load, failure occurs. The power supply produced a specified potential difference across the dolly, separation occurs. The measured pull-off force was used to calculate the adhesion strength. The above-mentioned aluminum dollys were used as electrodes to apply a direct electric field on PNIPA hydrogel. Each of the dollies was attached to one of the power-supply terminals. The power supply produced a specified potential difference between two dollies. Pull-off adhesion tests were carried out while the electric field was applied to the system. The electric field was found to be a factor reducing the adhesion strength of PNIPA hydrogel to the aluminum surface. Separating-force decrease was found to be proportional to potential-difference increase. Failure in an adhesion layer occurs on the surface of the cathode dolly. Based on data obtained, the electric field can be used to regulate the adhesion strength of PNIPA hydrogel. This ability to control the adhesion strength could lead to a new type of advanced adhesive.