Synthesis of Poly(4-vinylphenoxyphthalonitrile-*b*-styrene) Cobalt Dispersion Stabilizers using Stable Free-Radical Processes

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Abstract

The cobalt dispersion stabilizer poly(4-vinylphenoxyphthalonitrile-*b*-styrene) was synthesized using a combination of stable free-radical polymerization (SFRP) and chemical modification processes. Poly(4-acetoxystyrene) was synthesized using the unimolecular TEMPO initiator, 1-phenyl-1-(2’,2’,6’,6’-tetramethyl-1’-piperidinyloxy)ethane, and subsequently used as a so-called macroinitiator for the bulk synthesis of poly(4-acetoxystyrene-*b*-styrene) using SFRP. The pendant acetoxy groups were deacetylated to afford poly(4-vinylphenol-*b*-styrene), and the pendant phenols of this copolymer were subsequently derivatized with 4-nitrophthalonitrile to afford poly(4-vinylphenoxyphthalonitrile-*b*-styrene). The phthalonitrile block copolymer was used to form stable dispersions of cobalt nanoparticles approximately 10-50 nm in diameter. The cobalt-phthalonitrile copolymer complexes were subsequently pyrolyzed under inert conditions to afford cobalt nanoparticles with graphitic coatings.

Reactivity Studies of Nano-Crystalline MgO Filaments with Dimethyl Methyl Phosphonate, a Chemical-Warfare-Agent Simulant

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ABSTRACT

The study of organophosphate chemical warfare agents (CWA) and their simulants has become a growing area of research in the last decade. As the desire to destroy CWA stockpiles and the necessity to protect against them grows, researchers must investigate more efficient, yet practical, methods of destruction and decontamination.

Evaluation of a Beam on Elastic Foundation Design Method for Acrylic Foam Tape Bonds

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Abstract

In engineering design, the performance of structures depends upon the knowledge of the properties of the materials used. This study validates some of the factors of design proposed for use with VHB bonded structures. Characteristic to each structure are the flexibility of the materials bonded to the VHB as well as the type of load supported by the structure. This study investigated the strength of a wide variety of flexibilities and two types of loads. In general, the study found that factors of design for end loading were more accurate than design factors for center loading, but a factor of safety is still necessary in order to account for the statistical deviations. However, the effects of the 95% stress area on the theoretical predictions require more research.

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Fabrication and Performance Testing of Monopolar Plates for Fuel Cell Operation

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Abstract

Bipolar plates not only a have a tremendous effect on the performance of the proton exchange membrane fuel cell (PEMFC), but also on the cost. Finding ways to make production cost effective is essential to the commercialization of fuel cell technology. One way of fabricating composite plates is through the compression molding of graphite and polymer. The work discussed entails testing done on compression molded plates made from different combinations of graphite (TC300 and KS150) and polymer (polyethylene terepthalate (PET) and polyphenylene sulfide (PPS)). Tensile tests were conducted to determine the mechanical strength of the polymers. Thru and in-plane conductivity tests were used to asses which graphite provides better conductivity. DMA, TGA, and contact angle tests were also performed on the plates. With the completion of electrical, mechanical, and surface property tests an optimum composition was determined and used to make plates with flow channels to be tested in a PEMFC.

SYNTHESIS AND CHARACTERIZATION OF STAR-SHAPED POLY(D,L-LACTIDE)S

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Abstract

The synthesis and characterization of star-shaped poly(D,L-lactide) (PDLLA), proved an excellent learning experience in a laboratory setting. A series of high molecular weight (M_n) 4-arm stars containing an pentaerythritol ethoxylate (PTOLEO) core were synthesized for a collaborative study with Cathie Jones. These were characterized using size exclusion chromatography (SEC) and proton nuclear magnetic resonance (^{1}H NMR). The same shaped stars were also synthesized at lower M_n and the attempt was made to functionalized these with photocurable end groups. Some success was seen in the stars treated with isocyanatoethyl methacrylate (IEM), but none was evident in those treated with methacrylic anyhydride (MAAH). To show real-time analysis of the monomer concentration in a 4-arm star synthesis, *in-situ* fourier transform infrared spectroscopy (FTIR) ran continuously for 24 hours (h) during a reaction. The peak at 1244 cm^{-1}, attributed to the carbon-oxygen bonds in the monomer did, in fact, disappear. A series of 6-arm stars were synthesized using dipentaerythritol (DPTOL) initator, and these were also characterized using SEC and ^{1}H NMR.

The Kinetics of Morphology Development in Thermoplastic Polyurethanes

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Abstract

The morphology- time- temperature relationships in poly(tetramethyleneoxide) (PTMO) based segmented 1,6-Diisocyanate (HDI) urethane copolymers were investigated. Polyurethane was prepared with hard segment content of 14.72% by weight. Samples were prepared by hot pressing and solvent casting. The resulting hard- and soft-segment morphologies were characterized by using Fourier Transform Infrared Spectroscopy (FTIR) and atomic force microscopy (AFM). Hydrogen bonding interaction between hard and soft segments leading to a gradient interphase was studied between 30 and 60 °C using FTIR spectroscopy. Phase separation and phase mixing behavior of thermoplastic polyurethanes (TPUs) could also be followed by differential scanning calorimetry (DSC).

Keywords: Heterogeneous morphology; Hydrogen bonding; Segmented Polyurethane

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Nutritional Amelioration of Oxidative Stress Induced by Obesity and Acute Weight Loss

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Abstract

Obesity has become a common problem among companion animals. This study investigated the effects diet and acute weight loss over four weeks on levels of oxidative stress in cats by measuring biomarkers indicating oxidation of lipids, DNA, and protein. The two dietary treatments utilized in this study were a high protein-calorie restricted diet (HP) and a high carbohydrate-calorie restricted diet (HC). The study included a two hour oxygen stress on each cat to induce oxidative stress during week three prior to beginning the weight reduction period. Three assays were used as biomarkers of oxidative stress *in vivo* and included lipid peroxidation (LPO), 8-hydroxy-2’-deoxyguanosine (8-OHdG) to assess DNA damage, and $\propto_1$- antiproteinase ($\propto_1$-AP) to determine protein oxidation. The results showed that there was an effect of time on all oxidative stress parameters, but there was no significant treatment effect. There was one exception however; the urinary 8-OHdG values were significantly higher in the HC diet than the HP diet at the end of the weight reduction period.

Poly(dimethylsiloxane-*b*-2-ethyl-2-oxazoline) Copolymers as Potential Surfactants for the Formation of Silica-Cobalt Microspheres

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Abstract

Well-defined poly(dimethylsiloxane-*b*-2-ethyl-2-oxazoline) copolymers were prepared for use as surfactants for silica microsphere formation. Poly(dimethylsiloxane) was synthesized via living anionic ring opening polymerization and terminated with a benzyl chloride-containing chlorosilane. Poly(dimethylsiloxane)-benzylchloride macroinitiator was utilized for the cationic polymerization of poly(2-ethyl-2-oxazoline). DSC confirmed two phase nature of the surfactant in the solid state and dynamic light scattering studies showed the presence of micelles in a polar solvent (NMP). Solutions of trimethoxysilyl-containing copolysiloxanes and PDMS-*b*-PEOX in NMP produced 150 nm size silica-based microspheres as evidenced by TEM.

Blends of Amphiphilic Poly(dimethylsiloxane) and Non-Amphiphilic Octaisobutyl-POSS at the Air/Water Interface

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Title running head: Amphiphilic PDMS/Non-Amphiphilic POSS Blends
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ABSTRACT

Brewster angle microscopy (BAM) shows that a non-amphiphilic polyhedral oligomeric silsesquioxane (POSS) nanofiller, octaisobutyl-POSS, forms aggregates at all surface concentrations at the air/water interface. When amphiphilic poly(dimethylsiloxane) (PDMS) is blended with the octaisobutyl-POSS (> 10 wt% PDMS) the degree of aggregation dramatically decreases. Thermodynamic analysis and morphology studies through surface pressure-area per monomer isotherm data and BAM, respectively, exhibits three distinct composition regimes: 1) Blends with ≥ 80 wt% POSS have unstable isotherms whose shapes deviates from PDMS and form large rigid domains comparable to, but smaller than pure, octaisobutyl-POSS films; 2) At compositions between ≈ 30 and 70 wt% POSS, the isotherms' features are comparable to pure PDMS, and extensive nanofiller networks are observed by BAM; and 3) For compositions ≤ 20 wt% POSS, the isotherms are essentially those of pure PDMS with small POSS domains dispersed in the PDMS matrix. These results provide further insight into the nanofiller aggregation mechanisms and dispersion that may be present in thicker films and bulk systems.

pH Effects on Trisilanolphenyl-POSS Stability

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Abstract

Polyhedral oligomeric silsesquioxanes (POSS) have been an innovative area of intense study for the past two decades. In this study, trisilanolphenyl-POSS (TPP), a molecule known to form Langmuir films at the air/water interface, was examined for stability at various pH values. Isothermal and isobaric experiments using the Wilhemy plate technique along with Brewster angle microscopy (BAM) images were used to investigate the stability of TPP on buffered subphases. This study found that the stability of TPP decreased as the basicity of the subphase increased. As the TPP rested on the subphase, hydrolysis reactions broke siloxane bonds and dissolution into the subphase occurred.

Polymer-Cobalt Complexes and Their Conversion to Functionalized Nanoparticles

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Abstract:

Poly (4-vinylphenoxyphthalonitrile-co-4-vinylphenoxytriethoxysilane-g-dimethylsiloxane) copolymers have been synthesized using a combination of free-radical and chemical modification processes. The precursor for the graft copolymer, poly (4-acetoxystyrene), was free-radically polymerized using benzoyl peroxide. Deactylation of poly(4-acetoxystyrene) provided poly (4-vinylphenol) which was subsequently derivatized with 4-nitrophthalonitrile via nucleophilic aromatic substitution to generate poly (4-vinylphenol-co-4-vinylphenoxyphthalonitrile). Trivinylchlorosilane was then reacted with the copolymer to afford poly (4-vinylphenoxyphthalonitrile-co-4-vinylphenoxytrivinylsilane). The vinyl groups of this copolymer were hydrosilated with hydrido terminated PDMS and later triethoxysilane to produce the graft copolymer poly (4-vinylphenoxyphthalonitrile-co-4-vinylpheoxytriethoxysilane-g-dimethylsiloxane).

The graft copolymers were used to form stable ferrofluids of cobalt nanoparticles via the thermolysis of $Co_2(CO)_8$ in solutions of toluene. The cobalt-graft copolymer complexes were pyrolyzed at 700 °C to afford cobalt complexes coated with a combination of graphitic and silica char. The silica coatings were subsequently coupled with 3-aminopropyltrimethoxysilane to afford amine functionalized cobalt nanoparticles.

Solvent Effects on the Rate of Decomposition of Dialkyloxyamines

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Abstract

A method for measuring the dissociation rate constants for dialkyloxyamines ($R_2NO\bullet$) as a function of solvent polarity was developed which employed the use of benzene thiol as a radical trap. The dialkyloxyamine 2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine (TEMPO-EtPh) was showed to exhibit little or no solvent effects over the range of solvents tested. Dissociation rate constants for TEMPO-EtPh at 110°C in a range of non-hydrogen donating solvents are reported.

Fabrication and Performance Testing of Monopolar Plates for Fuel Cell Operation

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Abstract

With the depletion of fossil fuels, the development of alternative energy sources has become a primary focus in the automotive and electrical industry. Fuel cells have shown to be a practical, efficient, and environmental friendly energy source. In effort to make fuel cells cost effective, industrial and academic research are currently concentrated on the advancement of composite bipolar plates to replace pure graphite plates. Eighteen different combinations of wet-lay material consisting of two types of graphite (TC-300 and KS-150), polyethylene terephalate (PET), polyphenylene sulfide (PPS), glass fiber and carbon fiber were fabricated. All samples were tested for mechanical strength, in-plane and through- plane conductivity, contact angle and surface energy, glass transition temperature (T_g), and thermal expansion. The plate containing TC-300 graphite, PPS, and carbon fiber was chosen for short-term fuel cell test to determine the energy efficiency of the novel composite plates in respects to industrial standards.

AMIKACIN RELEASE FROM ELECTROSPUN POLY(D,L-LACTIDE) FIBERS

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Abstract

Electrospun linear and 4-arm star poly(D,L-lactide) (PLA) nanofibrous scaffolds demonstrated successful incorporation and release of an antibiotic, amikacin. Analysis of a two week elution study using electrospun linear and 4-arm star PLA of different weight average molecular weights, M_W, ranging from 40 and 88 kg/mol impregnated with amikacin provided an amikacin release profile for the electrospun fibers. The amount of amikacin incorporated directly influenced the amount of antibiotic eluted. Further analysis showed that the topology of the PLA affected the morphology of the electrospun fibers as well as the maximum incorporation of amikacin into the electrospun scaffolds. As a result, the molecular architecture of the electrospun PLA directly influenced the amikacin release profile.

MECHANICAL BEHAVIOR OF NAFION® AND BPSH MEMBRANES

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Abstract

A brief characterization of the mechanical behavior of Nafion® 117 and BPSH-35 membranes took place through uniaxial loading, stress relaxation, and creep compliance tests. Membranes underwent uniaxial loading at various strain rates to observe yield and fracture behavior. Stress relaxation tests measured relaxation response to strain rate and relaxation strain. Creep compliance tests led to the formation of a creep master curve for the Nafion® membrane. Tests showed that for Nafion®, higher strain rates produced higher yield stresses and yield strains as well as faster initial relaxation. Strain rate had no effect on strain at fracture. Higher relaxation strains also led to faster initial stress relaxation in both Nafion® and BPSH. BPSH results showed no yield trends in uniaxial loading, though they illustrated lower breaking strains with higher strain rates.

Plasma Modified Polymer Electrolyte Membranes: Deposition of Platinum on Polysulfone Films for use in Fuel Cells

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Abstract

Sulfonated polysulfones (SPSu) are being developed as an alternative polymer electrolyte membrane to Nafion in fuel cells. Plasma deposition was explored as a method of adhering platinum species to the surfaces of sulfonated polysulfones and Nafion. A support of activated carbon, also treated via plasma deposition, was investigated as a means of improving film performance. An ink film was prepared for comparison. The treated polymer films were tested in a fuel cell, and compared in performance to the ink film. The atomic percent composition was determined via X-ray photoelectron spectroscopy. The 2-hour performance yielded a voltage of 0.894 V for the ink film, 0.847 V for the carbon-supported Nafion, and 0.79 V for the carbon-supported SPSu. When a load was applied to the fuel cell to measure the current, the presence of a carbon support increased the current from negligible in all unsupported films, to 57 mA at 0.27 V for a carbon-supported SPSu film and 65 mA at 0.24 V for a carbon-supported film.

SYNTHESIS AND CHARACTERIZATION OF THE COLLAGEN MIMETIC POLYPEPTIDE (Gly-ψ[(*E*)CH=C]-Pro-Hyp)$_n$ AND THE MODEL POLYPEPTIDE (Gly-Pro-Pro)$_n$

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Abstract

Collagen is the most essential protein polymer functioning as a major structural constituent in human body. Collagen as a biomaterial exhibits an excellent biocompatibility and safety due to its stable triple helical structure. To generate a stable, self-assembling material, the synthesis and characterization of a collagen mimetic polypeptide (Gly-ψ[(*E*)CH=C]-Pro-Hyp)$_n$ ((2S,4R,E)-1-(2-(2-aminoethylidene)cyclopentane- carbonyl)-4-(tert-butyldimethylsilyloxy)pyrrolidine-2-carboxylic acid) and its model (Gly-Pro-Pro)$_n$ ((S)-methyl 1-((S)-1-(2-(tert-butoxycarbonyl)- acetyl)pyrrolidine-2-carbonyl)pyrrolidine-2-carboxylate) were performed. The tripeptide monomers were synthesized starting from a single amino acid to examine the amide bond polymerization in polypeptide formation. Poly(Gly-Pro-Pro) was synthesized to simulate the general amide bond polymerization of the tripeptide monomer prior to polymerizing the mimetic monomer.

Immunofluorescent Analysis of Interleukin-1 Effects on Insulin-like Growth Factor Binding Protein-2 Levels on Articular Chondrocyte Surfaces

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ABSTRACT

Effects of varying concentrations of interleukin-1 (IL-1) on equine articular chondrocytes were analyzed. Immunofluorescence was used to quantify surface levels of insulin-like growth factor binding protein-2 (IGFBP-2) on treated cells. Results from this study were expected to correlate with overall binding protein levels determined in previous binding studies; however, trends did not match. Chondrocytes grown on tissue culture plastic were shown to exhibit no marked differences in IGFBP-2 levels; whereas chondrocytes grown in alginate bead culture and treated with IL-1 concentration of 1 ng/mL had significantly lower IGFBP-2 levels than those treated with 0 ng/mL and 10 ng/mL concentrations. Recommendations are given to improve accuracy and precision in results for repetitions of this study.

DURABILITY AND VARIABILITY OF FIBER-REINFORCED POLYMER (FRP) CONCRETE REINFORCING BAR

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Abstract

In an effort to prevent corrosion and extend the service life of structures, the use of fiber reinforced-polymer (FRP) reinforcing bars to replace steel bars increased with time. One of the many unknowns is the variability of FRP tensile properties. To develop a better understanding of the variability of FRP, the research described in this paper consisted of analyzing data from recent research, conducting test on bars extracted from two similar slabs subjected to different environmental conditions, and testing a lot of 20 unused FRP bars. For all the collected data, the average and standard deviation of the tensile strength and modulus of elasticity were calculated. Comparing the results of the extracted bars with the initial properties, the bars experienced an increase in the modulus of elasticity and a reduction in strength. All data was considered to determine that the factor of three times the standard deviation in the formula to calculate the guaranteed tensile strength (f^*_{fu}) of FRP rebar is very conservative. A Monte Carlo simulation was used to determine how the variability in properties of the FRP bars affects the failure of a beam or a slab with the passing of time considering no exposure and exposure to the environment. For both cases using the equation of FRP reinforcing ratio producing balanced strain conditions, rupture failures occurred (the bars rupture first instead of the concrete). In both cases when the balanced ratio is multiplied by 1.2 and 1.4 the expected failure would be crushing (the concrete ruptures first instead of the bar).

DESIGN AND TESTING OF ADHESIVELY BONDED FRP DECK JOINTS

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Abstract

Concrete infrastructures are being replaced by fiber reinforced polymers (FRP) in transportation construction. FRPs provide higher environmental resistance, less maintenance costs and faster installation processes. In this research experience, FRP samples simulating a bridge deck were tested to determine the joints strength towards a load. By optimizing the joints ratio we were able to maximize the load applied to the deck and minimize the decks stress. Five different joint types were tested for 4-point bending and fatigue; 15, 27, 30, and 45 degree scarf joint samples in addition to a 90 degree butt joint sample used for comparison.

Theoretically and experimentally the 15 degree scarf angle provided smaller stresses due to the larger area of inclination between joints, therefore this characteristic will present better bonding. In comparison to the 90 degree joint sample, the 15 degree scarf sample sustained larger loads and presented higher displacement values. In the fatigue test, the 27 degree scarf sample was tested; the data presented is scattered due to different bonding methods and the level of difficulty when applying the adhesive. Finally, each sample was modeled using ANSYS computer simulation program; this provided us with theoretical deflection values and maximum loads values used for comparison.

FATIGUE VARIABILITY OF E-GLASS/510-A-40 LAMINATES

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Abstract

The effective use of fiber reinforced polymer (FRP) composites in civil and naval applications requires the investigation of how the resistance of these materials changes with time, loading, and environmental conditions. Because testing for each material and situation is costly and difficult, a method of computing or simulating the degradation in the material is under development. This study aimed to characterize the fatigue variability of a woven pseudo quasi-isotropic E-glass vinyl ester composite in an effort to provide the necessary data to develop such a simulation. This paper reports on the analysis and results from strength and fatigue tests performed on a E-glass/510-A-40 laminate. A computer model was created to predict the remaining strength distribution of the composite, based of the initial material property distributions. The comparison of experimental and simulated results shows the simulated α and β parameters primarily fall within a 95% confidence interval of the experimental values. The simulation will be refined using the data from this study to create a more accurate representation of the material behavior.

EVALUATION OF THE DURABILITY OF FIBER-REINFORCED POLYMER REINFORCING BARS FOR CONCRETE THROUGH FIELD TESTING

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Abstract

Glass fiber-reinforced polymers (*GFRP*) are the most commonly used bars for civil engineering applications. In this project the behavior of these bars in the bridge construction is examined. One of the purposes of this project is static and dynamic load testing to determine the dynamic load allowance and the load distribution factor for two simple supported, 45 ft long, composite-slab-and-steel-girder. The first span (Span A) has GFRP bars as top mat reinforcement while the second (Span C) has all steel reinforcement. Dump trucks loaded with gravel were used to do the tests. Both end spans of the deck (A and C), were tested doing ten quasi-static tests (five close to rail and five straddling Girder 4), and five dynamic tests straddling Girder 4 on each span. The second purpose is the measurement of the deformations in the *GFRP* bars due to the loads applied and the field conditions exposure one year after the installation of the bridge. The data is compared with that obtained in the post-installation live-load tests of the bridge and the American Association of State Highway and Transportation Officials (AASHTO) Standard Specifications.

The results show that the GFRP bars do not change significantly in one year. But from the results there can be seen a relation between the stiffness of the decks and the dynamic load allowances. In addition, recommendations are made about the method used in the calculation of the impact factors.

Effect of Post Cure on Dow Chemical's Derakane 470-300 Vinyl Ester Resin and Vetrotex E-Glass Composite Panels Fabricated by Vacuum Assisted Resin Transfer Molding

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ABSTRACT

Composite panels are advantageous alternatives to the demand for machined metal products. They are light and resist corrosion in comparison to metal components. One major disadvantage is the change of mechanical properties over time. In order to help create a commercially ready product, vacuum-assisted resin transfer molding (VARTM) and post curing of panels has been used. For one resin, Dow Chemical's Derakane 470-300, only a wet lay up has been attempted to fabricate a composite panel. In order to reduce the amount of resin used and increase the number of bonds in the panel, VARTM is being inspected as a new way to fabricate a composite panel. The objectives of this project were to both fabricate FRP composite panels consisting of Dow Derakane 470-300 resin and Vetrotex 324 E-Glass woven fiber, and to compare the mechanical properties of composites post cured to five different temperatures.

Investigation of the Molecular Recognition Characteristics of Adenine Modified Silicon Surfaces

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Summer Undergraduate Research Program 2004

Abstract:

Silicon surfaces were modified with adenine functionalized triethoxysilanes. The attachment of adenine to surfaces was confirmed by X-ray photo electron spectroscopy (XPS), contact angle goniometry, fourier transform infrared spectroscopy (FTIR), and ellipsometry. In order to investigate the molecular recognition characteristics of such adenine modified surfaces, their reversible attachment to thymine-functionalized polymers was attempted. Since the adenine-thymine recognition relies on H-bonding, such adenine-modification leads to robust surfaces capable of attaching to a variety of molecules containing the complementary groups. To test this, a hydrophobic PS-thymine and a hydrophilic PEG-thymine were used in the study. The attachment of these polymers was studied by the above mentioned techniques. The stability of such an interaction to varying solvent polarity was also investigated.

VARIATIONS OF PERFORMANCE ON EPOXY USED FOR STEEL COATING AS A FUNCTION OF DIFFERENT TEMPERATURE AND BAKING TIMES

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Abstract

The corrosion of reinforcing steel is one of the major causes of deterioration in civil engineering structures. Epoxy-coated reinforcement (ECR) is the most common type of steel protection against corrosion used in the United States. It has been observed from cored samples that after some service time epoxy degradation is visible: peeling, debonding, color change, loss on the elastic properties, cracking, and steel corrosion can be seen. It is tough that the properties of this material can be enhanced by changing some variables in the coating process. This process was duplicated and variables on the coating and curing such as temperature and baking time were changed to see how the material behaved. Moisture diffusion tests were performed to samples with different baking times to establish if this has something to do with the final protection qualities. Also the glass transition point (Tg) for different baking times was obtained.

The results showed that moisture absorption is related with bake time at a fixed temperature. Greater times showed a decrease in water absorption leading to a better protection against water uptake. Baking time affected the Tg of the material which increased with lower baking times. In addition, recommendations are given to improve the manufacture process from the laboratory observations on the sample.

SYNTHESIS & CHARACTERIZATION OF NOVEL CATIONIC POLYMERS BASED ON PHOSPHONIUM SALTS

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Abstract

The synthesis and characterization of novel phosphonium salt containing monomers and polymers as potential gene transfer agents is described. The monomers synthesized include: trioctyl(vinyl)phosphonium bromide monomer, 2-(hyrdoxyethyl)phosphonium bromide precursor, and a phosphonium salt containing methacrylate monomer. Using these monomers, homopolymers and copolymers were synthesized using free radical polymerization techniques. Both monomers and polymers were characterized using proton nuclear magnetic resonance spectroscopy (^{1}H NMR). Polymers and copolymers were characterized using size exclusion chromatography (SEC) and differential scanning calorimetry (DSC). Matrix assisted laser desorption – time of flight (MALDI-TOF) analysis was used to characterize the 2-(hyrdoxyethyl)phosphonium bromide precursor, and Fourier transform infrared spectroscopy (FT-IR) was utilized to monitor the phosphonium salt containing methacrylate monomer synthesis. Neither polymers nor copolymers were water soluble and therefore are not applicable as gene transfer agents. It is thought that the octyl groups form micelles in water and are therefore inhibiting water solubility. Despite this, SEC data for both polymers and copolymers shows relatively substantial molecular weights, which may lead to significant physical properties. Although these polymers are not applicable as gene transfer agents they could potentially be used in other applications such as polymer clay nanocomposites.

Keywords: phosphonium salt polymers, gene transfer agents, water soluble

TEMPERATURE-DEPENDENT THERMAL DIFFUSIVITY OF GLASS/VINYL ESTER COMPOSITE

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Abstract

This study examines thermal parameters, namely diffusivity, specific heat, and conductivity, in a glass/vinyl ester polymer composite over a range of temperatures from 20°C to 150°C. Testing determined thermal properties through the thickness and in the 0° and 90° in-plane dimensions of the E-glass/Derakane 510-A-40 VARTM composite. Transient thermal conditions were generated through pulse heating of the 0.203 m by 0.203 m (8 in by 8 in) specimen. Diffusivity values were determined from temperature response histories using Fick's Second Law of Diffusion, specific heat by Kubicar's method based on energy input and a temperature peak, and conductivity through a relation of diffusivity, specific heat, and density. Diffusivity was found to decrease with increased temperature, while the behavior of specific heat was tied the glass transition temperature of the material. Conductivity exhibited a less evident trend over the range studied.

Synthesis and Characterization of Sulfonated Poly (arylene ether sulfone) Copolymers with Pendent Sulfonic Acid Groups

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ABSTRACT

Sulfonated poly(arylene ether sulfone) copolymers with pendent sulfonic acid groups were synthesized by the direct copolymerization of methoxy-poly(arylene ether sulfone) (MHQS-XX, where XX represents the mole percentage of methoxy groups), then converting the methoxy groups to the reactive hydroxyl form (HOHQS-XX), and finally functionalizing the ydroxyl form with pentafluorobenzene sulfonic acid. These copolymers were characterized by intrinsic viscosity (I.V.), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. The I.V. and glass transition temperature (T_g) both increased in the conversion of MHQS-XX to HOHQS-XX due to an increase in intermolecular interactions. However, there was no change in the TGA data between the two copolymers. There was a change in the TGA data between the HOHQS-XX and the sulfonic form (FHQS-XX). The FHQS-XX decomposed faster due to the introduction of sulfonic acid groups in the copolymer. In addition, FHQS-30 copolymer had an inherent proton conductivity of 0.008 S/cm, which compared well to similar systems prepared by direct copolymerization.

Modifying pH of biomimetic PAH/Heparin films to alter cell proliferation and osteoblastic differentiation

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Abstract

The interaction of cells and substrates affects development in both *in vivo* and *in vitro* environments. To study this relationship, representative surfaces were prepared with polyelectrolyte films of heparin and poly(allylaminehydrochloride) (PAH) in a layer-by-layer assembly process. Different coatings were prepared by varying pH of polycationic solutions to create six distinct types of films with differing topmost polymers and surface chemistry. The chemistry of the films was evaluated using water contact angles measurements. Similar protein absorption was found using ^{125}I-fibronectin. Rat bone marrow stromal cells (BMSCs) and mouse MC3T3-E1 cells were cultured on these films to determine their effect upon osteoblastic proliferation and differentiation. MC3T3-E1 cells grew better than BMSCs on all surfaces. Additionally, alkaline phosphatase activity, a measure of extracellular matrix development, showed no significant trends with varying pH. Protein analysis of osteopontin (OPN), a bone specific protein, showed all surfaces contained similar or greater OPN levels as cells grown on tissue culture polystyrene except heparin-topmost films created with alternating PAH of the highest pH. This study indicates that conditions of formation for polyelectrolyte biomimetic films can significantly affect the surface chemistry and influence the differentiation process.

CATIONIC POLYELECTROLYTES AS GENE TRANSFER AGENTS: TOPOLOGICAL AND MOLECULAR WEIGHT EFFECTS ON POLYPLEX SIZE

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Abstract

Cationic polyelectrolytes, as gene transfer agents, facilitate genetic material across cellular membranes by binding to plasmid DNA through electrostatic interactions forming a polymer-plasmid complex or polyplex. Through this adhesion, plasmid size is condensed. Considering that a smaller neutralized molecule has a great probability of surpassing the cellular membrane, plasmid size condensation is a considerable advantage. The effects of polymer topology and molecular weight were studied though the conventional free radical polymerization of the water soluble cationic polyelectrolytes of poly(2-dimethylaminoethyl methacrylate) (linear PDMAEMA) and poly(2-dimethylaminoethyl methacrylate-*co*-polyethylene glycol dimethacrylate) (branched PDMAEMA). The effects of molecular weight on polyplex size and transfection efficiency were evaluated through the stable free radical polymerization of poly(2-dimethylaminoethyl acrylate) (PDMAEA). Characterization of the polyelectrolytes complexing to the plasmid pCMVnt-lacZ (polyplexes) were carried out through dynamic light scattering (DLS), atomic force microscopy (AFM), and tunneling electron microscopy (TEM). The results suggest that linear and branched PDMAEMA condense plasmid size more effectively relative to PDMAEA. In comparative transfection studies utilizing the immortalized cell line COS-7, a 4 to 1 polymer to plasmid weight to weight (w/w) was held constant, whereas, the polymer concentration was varied between 6.25 µg/mL to 100 µg/mL. Depending on the assay and characterization test (DLS, AFM, TEM), linear and branched PDMAEMA varied as to which gene transfer agent transfected and condensed plasmid size more effectively. At all varying molecular weights, PDMAEA did not transfect or condense plasmid size efficiently. Based on these finding, molecular weight does not appear to have as a dramatic of an impact on polyplex size condensation and transfection efficiency relative to polymer topology.

Key Words: gene transfer; gene delivery; cationic polymers; plasmid DNA; transfection; β-galactosidase; polyplex

SYNTHESIS OF SLIP-LINK MONOMERS FOR POLYROTAXANES

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Abstract:

An attempt was made to synthesize 6,6-carbon monomers for slip-link polyrotaxanes. *p*-(6-Hydroxyhexyloxy)benzaldehyde has been synthesized. Also, *p*-(6-hydroxyhexyloxy)benzonitrile has been synthesized and characterized. The synthesis of the 6,6-carbon monomer slip-link has not been completed.

Compression Strength of E-Glass/Vinyl Ester Composites under Isothermal Conditions

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Abstract

Several isothermal tension tests were performed on woven $[\pm 45]_{2s}$ E-glass/vinyl ester composites in order to gather data to be used in the Budiansky and Budiansky-Fleck compression strength models. These composite materials, fabricated using the vacuum-assisted resin transfer molding (VARTM) process, produced hard-to-interpret results at temperatures above the glass transition. Compression testing was then performed on $[90]_{10}$ and $[0]_{10}$ laminates to determine the actual strengths of the material, which were compared to the predictions in order to determine the accuracy of the models. This comparison shows that the test results fall in between the predictions of the Budiansky and Budiansky-Fleck models.

The Characterization and Comparison of Whey Protein Film Properties and Film Effectiveness in Preventing Rancidity in Roasted Peanuts

by
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ABSTRACT

Cast whey protein isolate (WPI) films were characterized and applied as edible coatings to inhibit peanut oxidation. The concentrations in the cast films were: **1**) 6% WPI; **2**) 6% WPI, 4.8% sorbitol; **3**) 6% WPI, 4.8% sorbitol, and 0.2% butterfat (lipid); **4**) 6% WPI, 4.8% sorbitol, 0.2% lipid, and 2% α-tocopherol (Vitamin E). Films exhibited similar pH and water vapor permeability properties. The 6% WPI film was brittle due to no plasticizer. The 6% WPI and 4.8% sorbitol film had higher puncture and tensile strengths than other films. Peanuts were coated with the following solutions: **1**) No coating (control); **2**) 6% WPI, 4.8% sorbitol, and 0.2% butterfat; **3**) 6% WPI, 4.8% sorbitol, 0.2% butterfat, 0.5% trolox, and 1% α-tocopherol; **4**) 6% WPI, 4.8% sorbitol, 0.2% butterfat, and 1% trolox; **5**) 6% WPI, 4.8% sorbitol, 0.2% butterfat, and 1.5% α-tocopherol. The 1% trolox and the 6% WPI, 4.8% sorb, and 0.2% lipid coatings effectively controlled peroxide values in peanuts at accelerated conditions. The 1.5% Vit E coating functioned as a prooxidant, having the highest peroxide value under accelerated conditions. Overall, the whey protein isolate films may control oxidation in peanuts.

KEY WORDS: Whey protein films, mechanical properties, physical properties, trolox, α-tocopherol, antioxidants, edible films, oxidation, peanuts