STATE OF THE ART PAPER: BIOMIMETICS: ADAPTING PERFORMANCE AND FUNCTION OF NATURAL MATERIALS FOR BIOBASED COMPOSITES

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(Received August 2012)

Abstract. Natural materials may serve as an excellent template for the design of high-performance manufactured materials. Because natural materials are fabricated at standard temperature and pressure from benign chemicals, adapting or mimicking nature’s design methods and structures offers the potential to enhance performance, lower energy requirements, decrease toxic chemical accumulation, and create materials with life cycles that better correspond with the environment. As the forest products industry has matured, adapting naturally occurring designs has meant potential innovation for commodity markets, decreasing manufacturing inputs (energy, carbon, or other materials), and enhancing product performance. This study reviews nature-inspired pathways for biocomposites to 1) enhance the specific mechanical properties, 2) assemble materials from aqueous systems, 3) create hybrid inorganic–biopolymer composites, and 4) develop functional hydrophobic coatings and photonic colored films. To achieve controlled architectures found in natural materials, innovative production technologies that allow for timed processes and self-assembly must be applied to biobased composite manufacturing.

Keywords: Biomimetics, biomimicry, biocomposites, foams, polymer composites, biomineralization, iridescence.

INTRODUCTION

Scientists have recognized that motifs found in natural materials offer the organism a level of functionality and performance that is very difficult to reproduce in synthetic materials (Bhushan 2009). The study of the structure and composition of natural materials, at varying length scales, can serve as a guide to enhance the properties of manufactured materials (Bond et al 1995). After unlocking these natural “secrets” that offer functionality, the architectures usually can be duplicated in the laboratory, achieving similar performance from the resulting material, eg synthetic analogs to the gecko foot. The field of biomimetics, loosely defined as adapting the design process from naturally occurring structures and mechanisms (eg texture of a lotus leaf for superhydrophobicity or the structure of spider dragline silk for strong fibers), can significantly impact the manufacturing of composite materials (Reed et al 2009). This approach is paradigm changing, shifting away from iterations of tweaking current materials and manufacturing processes for slight improvements. Biomimetics as a design tool focus on the structure or process that was optimized across millennia for the needed performance of the organism. Because this performance was critical to the organism’s survival, failed designs disappeared. Determining the mechanisms of how biopolymer materials have been able to meet performance with unique micro- and nanoarchitectures, augmented by incorporation of minerals in some cases, provides a pathway toward rational composite design based on optimized models.
COMPOSITE DESIGN

Assembling Lightweight Structured Polymer–Polymer Materials as in Nature

Natural materials possess excellent mechanical properties relative to their mass. Hence, one physical property that differentiates natural materials from synthetic materials is density. Natural materials are light compared with the majority of materials from the industrial revolution (bricks, engineering steel, and glass). Glass and metals, which make up a large percentage of society’s materials, have densities between 2 and 20 mg/m³. Soft tissues found in natural materials (i.e., spider silk, collagen, keratin, wood) have a fraction of the density of these materials, typically about 0.3 to 1.5 mg/m³. Natural materials such as plants are light because they are derived from light reactants such as carbon dioxide, water, and gaseous nitrogen compared with silicon, iron, and aluminum. Also, many natural materials such as wood, bone, and even beak are extremely light because of their cellular nature. The toucan beak is more than 1/3 the length of the bird, however the foamed keratin structure only weighs 1/20 of the bird’s mass (Seki et al 2005). Lighter beaks and bones require less energy input from the organism for locomotion, just as weight decrease of a vehicle enhances fuel efficiency.

Ordered structures within the cellular walls of natural materials contribute to the high performance of these naturally occurring foams (Fratzl and Weinkamer 2007). Typically, synthetic polymer foams (i.e., polystyrene foam) do not achieve the same ordered structure found in natural materials. For example, cellulose microfibers are oriented within the secondary cell wall of woody tissue. To mimic in-plane orientation of the cell wall, Svangen et al (2007, 2008) were able to use a simple method involving lyophilization based on an aqueous suspension of cellulose microfibers and starch to form highly ordered foams. This structure is similar to the cell wall with fibrils ordered within the plane of the ligament (wall of the cellular foam), albeit without controlled axial orientation as in wood cells. The method was used with material combinations of nanoscale clays and cellulose (Gawryla et al 2008). As the suspension of nanoparticles freezes, ice crystals begin to exclude solute (or dispersed particles) resulting in the orientation of these materials between ice crystals (Gawryla et al 2009). These studies show effective ways to build cellular structures in processes that can produce bulk-scale materials with intimate control of structure. In addition to decreasing weight, the high percentages of void volume (99.5% in some cases [Sehaqui et al 2010]) provide the potential for excellent thermal insulation properties. The key to the biomimetic design of cellular materials is to have multiple levels of order from the microscopic cellular nature to the nanoscale organization of nanoparticles, as demonstrated by the lyophilization method (Svagan et al 2010). Another technique uses templating of microspheres to form foams with ligaments with ordered nanoparticles (Zhang and Cooper 2005). In a simplified model, the expanding cell lumen has a cytoplasmic membrane with a secondary wall templated on the interior of the primary wall. It is actually common practice to template sintered spheres and remove the template to create low-density lightweight materials. This method provides a greater degree of control of the microscale structure within the foam. Blaker et al (2010) used an approach that combined both lyophilization and templating; bacterial cellulose nanowhiskers were mixed with polylactic acid and subsequently templated on the surface of ice microspheres. After solvent removal of the matrix polymers, the samples were lyophilized and the 3-D structure with controlled pore size was isolated.

These foams used biobased nanoparticles that contain inherent organization at multiple-length scales. These levels of organization are assembled from the molecular level up to the microscale level. Correspondingly, this scale of order covers the detail related to polymer structure. Structural polymers within organisms are derived from building block intermediates such as carbohydrates and amino acids that repeat in
a way that allows for specific agglomeration, folding, and assembly. These natural polymers are simple in composition because they contain few elements—plant-based polymers only have carbon, hydrogen, and oxygen in the majority of their structures, whereas protein-based materials also have nitrogen, sulfur, and occasionally selenium. However, although simple in composition, there are many different ways to assemble these atoms, providing a complex array of possible primary structures. For example, starch, cellulose, and pullulan are polysaccharides derived from the building block glucose. Their linkage types are different for these glucans creating a difference in structure. Nature has narrowed down the linkages that offer the highest degree of structural reinforcement and the linkages that lead to easy breakage to access glucose as an energy reserve. Hence, the molecular structure (bonding patterns of the atoms) within the polymer dictates the organization that can be used for structural polymers, such as cellulose, or energy reserve polymers, such as starch. Cellulose molecular structure dictates assembly into fibrils with its cellulose chains aligned along the particle axis for full axial reinforcement. For cellulose, individual chains are assembled in sheets as they leave the terminal complex synthase. These sheets are stacked together to form ordered fibrils with defined symmetry (Doblin et al 2002; Saxena and Brown 2005). Tendon, a structured collagen material, has a similar hierarchical structure in which three tropocollagen polymer chains are assembled into larger microfibril structures. These fibrils are assembled into larger ordered fibers at different stages and are oriented along the axis of the tendon (Baer et al 1992). This structure is significant because it allows for self-reinforcement, orientation, and prevents crack propagation (Brown et al 2012).

Natural polymers themselves do not have special properties except inherent stiffness because of ring structures (ie pyranose and phenol propanol) and chemical functional groups (ie amines, carboxylic acids, and hydroxyls). In fact, reprocessing these materials will degrade the majority of the performance characteristics found in the natural material—recombinant spider silk does not give tenacity equal to drag-line silk (Lazaris et al 2002), keratin does not have the same strain to failure as a feather (Aathamneh et al 2008), and the ultimate tensile breaking strength of rayon fiber (cellulose) is much less than that of a cellulose wood fiber (Eichhorn et al 2001). These examples reveal that performance is not dictated solely by composition. Instead, additional levels of order are required for enhanced performance in materials. In these materials, structure is created in cellular environments that involve highly organized events in which intermolecular interactions play a key role in assembly of secondary and tertiary structures of the polymers.

One manufacturing process for developing composites with multiple levels of order is to begin with natural polymers already structured and only partially modify the structure during manufacturing. A simple route is to only partially dissolve semicrystalline materials; the crystaline cores are not disrupted, but surface chains are modified creating moldable materials. This technique was used to create all-cellulose composites from bacterial cellulose that had tensile strengths of 411 MPa and stiffness of 18 GPa (Soykeabkaew et al 2009). Also, filter paper showed a 4-fold enhancement of strength to 200 MPa when the surfaces of the fibers were selectively dissolved to form the “matrix” material while retaining the crystalline cores (Nishino et al 2004; Nishino and Arimoto 2007). These values are similar to what is found for glass-reinforced composite materials. Overall, retaining the supramolecular structure of the biopolymers enhances performance as the modulus/strength is increased relative to processed samples that did not retain their native crystalline cores. Another similar route is to heterogeneously modify the cellulose microfibril surface making heat-moldable samples while still retaining the unmodified crystalline core (Matsumura et al 2000).

Order can be induced into solid fibers and films by having the polymer solution in an organized state during processing. Drag-line silk from
spiders has levels of structure that provide the fiber a specific strength and stiffness stronger than steel fiber (Omenetto and Kaplan 2010). In the case of spider silk, there is liquid crystalline protein solution that orients as the filament is spun from the spinneret (Viney 1997). Molecular order is induced along the fiber that includes alternating tertiary structures of proteins (alpha helices and beta sheets) creating a series of structures with different mechanical properties that allows for enhanced toughness. Certain cellulose derivatives and isolated cellulose nanoparticles can also undergo liquid crystal formation in solution, which can be further processed into ordered solid materials (Dave and Glasser 1993). Lignin can help nucleate this phenomenon for cellulose ester solutions (Rials and Glasser 1989). Whereas most of these polymer solutions require toxic solvents, spider silk processing shows that water-soluble proteins can be oriented and spun, subsequently becoming insoluble after formation. This case demonstrates that there is room for improvement for spinning biopolymers from less environmentally burdensome solvents (Viney and Bell 2004). However, Iwamoto et al (2011) have shown that nanocellulose aqueous suspensions of oxidized fibrils can be wet-spun into fibers with orientation induced by increasing spinning rate. These fibers can reach a tensile modulus of almost 24 GPa and breaking strength of 320 MPa.

In addition to spider silk, most natural polymers are assembled in aqueous solutions and are insoluble after assembly. By exploiting intermolecular interactions and timed events, it is possible to build organized films of polymers or nanoparticles from aqueous solutions or dispersions that can begin to resemble natural tissues. Tang et al (2003) reported mimicking the seashell material, nacre, through the layer-by-layer (LbL) assembly process. Intermolecular interactions were exploited in this process with highly controlled deposition of thin layers of polymers (single digit nanometers) through sequential adsorption of oppositely charged polymers and/or nanoparticles (Decher 1997) (Fig 1). The technique has been adapted to cellulose nanocrystals (Podsiadlo et al 2005), lignin (Pillai and Renneckar 2009), hemicelluloses (Elazzouzi-Hafraoui et al 2008), and proteins (Lvov et al 1995), among other materials. The technique allows almost any surface to be used as a substrate—with examples such as glass, wood (Renneckar and Zhou 2009), cotton fiber (Dong and Hinestroza 2009), wood fiber (Lin et al

Figure 1. Principle of layer-by-layer modification of wood pulp fiber surfaces with solutions of polyelectrolytes. Because of surface charges, oppositely charged polyelectrolytes or nanoparticles adsorb on surfaces of substrate when treated in sequential order. Cycles can continue creating multiple layers.
2008), cellulose acetate films (Mamedov and Kotov 2000), and even stable air bubbles (Winterhalter and Sonnen 2006). For wood and fiber surfaces, the deposited films served as an adhesive layer (Zhou et al 2010) and have been used to create functional materials such as electrically conductive paper (Agarwal et al 2006). As a result, wood and fiber can be modified using simple systems along with controlled layers of wood-derived polymers or other additives that modify properties.

In addition to the LbL method, assembly in aqueous environments can be driven by the surface-active nature of the molecule, in which the molecule is partially polar and partially nonpolar. This method of assembly is the principle behind the cell membrane formation creating a regulated environment for cell processes to occur. As previously mentioned, the cell wall of wood is templated within a cellular environment, but there is further organization and blending of materials during tissue formation. Within the cell wall of wood, cellulose microfibrils are deposited in the presence of a collection of hetero-polysaccharides commonly referred to as hemicelluloses. These materials are often partially acetylated and absorb in thin layers on cellulose. Attempting to mimic a cellulose–hemicellulose layered structure, Gradwell et al (2004) measured the assembly of model cell wall polysaccharides on cellulose surfaces. Across a few nanometers, the nature of the cellulose surface was transformed with substituted polysaccharide that could interact with another matrix material. To achieve modification, the adsorbing polymer must be partially hydrophobic (Kaya et al 2009). In other words, the polysaccharide assembly in aqueous environments is not driven by hydrogen bonding (Fig 2). In fact, Kaya et al (2009) created model systems that began to mimic the interfacial area with wood-like polymers. When materials were deposited in thin layers, bulk properties of the materials began to change and the system was driven toward interfacial interactions with different phases forced to interact in narrow domains. Liu et al (2005) showed how this loss of the bulk phase caused two distinct nonmiscible polymer blends to behave as a miscible blend (in technical terms, this is a shift in glass transition of polymers) using folded melt blends of polymers. In wood, there are distinct domains of cellulose, but across only a few nanometers, there is a close association with the hemicelluloses and lignin (Terashima et al 2009) (Fig 3).

A third approach to creating polymer–polymer composite materials similar to natural materials is to mimic the mechanisms involved in adding a polymer to an existing template. For woody tissues, a lignin matrix seals the polysaccharide scaffolding that includes the cellulose microfibril and hemicelluloses. The process occurs external to the cytoplasm of the cell; phenolic monomers undergo oxidative coupling via enzyme-catalyzed pathways within the polysaccharide scaffold. Model systems incorporating this

Figure 2. Surface modification of cellulose with a water-soluble polysaccharide modified with hydrophobic cinnamate groups. Left image shows monolayer surface coverage based on concentration; right image shows atomic force microscope image of modified cellulose surface. Reprinted with permission from Kaya et al (2009) (© 2009 American Chemical Society).
strategy encompass enzyme-catalyzed polymerization of phenolic monomers within the presence of polysaccharides. Early work on the subject showed how the substrate impacted the resulting polymer structure (Siegel 1957). That work was followed up recently showing how the substrate controlled the superstructure of the lignin-like polymers (Micic et al. 2004). Nanoscale cellulose particles have provided a route toward dispersible fibrils on the same size scale as native cellulose. Typically, it is difficult to achieve good dispersibility of nanoparticles in polymer matrices without mechanical input. Following nature’s method of composite formation, Li et al. (2010) used oxidized cellulose microfibrils dispersed in an aqueous system and polymerized phenol monomers via horseradish peroxidase and hydrogen peroxide around the cellulose fibrils. The resulting composite material possessed evenly dispersed nanoparticles within the phenolic polymer. Unlike the control material without cellulose, the composite material was no longer soluble in simple organic solvents, similar to woody tissue. This approach was also used with functional carbon nanotubes to form nanocomposite materials that contained excellent dispersion of nanoparticles within the phenolic polymer material (Peng et al. 2009). Other studies used templates such as bacterial cellulose hydrogels inside dialysis membranes to control the diffusion of monomers (Touzel et al. 2003).

Cellulose nanoparticle suspensions can be concentrated into gels that have abundant particle–particle interactions. Once this gel is created, polymer matrices can be dissolved into a variety of solvents and the solution is exchanged into the nanoparticle gels. Solvent exchange techniques with hydrophobic polymers, such as polystyrene or polybutadiene, have allowed the creation of a number of unique nanocomposites with a percolating fibril network (Capadona et al. 2007). For some of these systems, the mechanical properties are reversible by more than an order of magnitude (20-800 MPa) when immersed in water. The particle–particle hydrogen bonding within the fibril network is switched off by exposure to water. This process mimics the structural concept of the property-changing sea cucumber, which can quickly change the modulus of its skin when threatened (Capadona et al. 2008). In summary, these studies show routes toward nanocomposite creation to get the full potential of the reinforcement. The processes usually occur near room temperature without the need for high-energy processing or toxic solvents in many cases.

**Assembling Hard Materials as in Nature: Mineralization of Biopolymers**

Hard natural materials such as bone, tooth, and shell actually have a bulk density much lower than synthetic ceramics, as well as enhanced fracture resistance. Hard materials in nature,
such as tooth enamel, bone, ivory, seashell, diatoms, and antler have calcium, sodium, silicon, and phosphorous compounds. These elements are arranged in specific patterns with other elements such as oxygen, carbon, and hydrogen generating crystalline planes of atomic symmetry. Calcium carbonate and hydroxyapatite are typical minerals within natural ceramics that are related to seashell and bone, respectively. The process of mineralization can augment material properties to enhance performance. For collagen materials, a difference in function between bone and tendon is notable; a difference in performance between synthetic hydroxyapatite ceramics and bone is notable as well. The latter does not have the same degree of fracture toughness (TenHuisen et al 1995), indicating it is not the presence of a particular component but the placement within the structure that matters. Intimate mixing of the components is required to achieve desired performance (Rho et al 1998) (Fig 4). If isolated collagen and hydroxyapatite particles were combined, the performance of the mixture would be poorer than that of bone because the structure would be significantly different (Tampieri et al 2003). An analogy is found in the cell wall formation in wood. Isolated lignin itself is characterized as being highly brittle. However, lignification occurs at cell wall maturation, synergistically reinforcing the polysaccharide scaffolding between the lamella of the secondary cell wall. A parallel system is found for protein–mineral materials in which the nanoscale inorganic component such as hydroxyapatite is nucleated and assembled at specific sites within the collagen extracellular matrix (Weiner and Traub 1992). These systems ensure the maximum extent of interfacial contact among domains forming hybrid properties that are different from the individual bulk materials.

Specific chemical groups nucleate mineralization on biopolymer structures. Ionic functional groups along the collagen fibril assist in the bone mineralization by nucleating growth of hydroxyapatite crystals from the surrounding calcium and phosphate-rich fluids. Translated to biomimetic composites, ionic functional groups introduced to the surface of synthetic fibers can induce mineralization into electrolyte solutions. A solution that mimics the composition of blood serum, simulated body fluid (SBF), was developed by Tas (2000). This area of work has been well studied to engineer tissue scaffolds for bone repair options. Modified scaffolds with COOH, PO₄H₂, OH, and SO₃H, have all been used to induce mineralization. On model surfaces, anionic groups tend to mineralize at the fastest rate, and this is related to their ability to bind calcium (Liu et al 2006). For cellulose-based fibers and scaffold, there are a number of methods to introduce these functional groups because the surface hydroxyls are readily modified by chemical means. Wan et al (2007)
phosphorylated bacterial cellulose hydrogels and found drastic improvement in hydroxyapatite growth relative to unmodified cellulose without the anionic phosphorate esters.

Also, modification by polymer adsorption offers a noncovalent modification route toward functionalization. Based on modification of model cellulose surfaces regenerated from trimethylsilyl cellulose (Liu et al 2011) with carboxymethylcellulose (CMC) and calcium chloride, Zimmermann et al (2011) modified bacterial cellulose with this method to induce hydroxyapatite formation. A similar route of CMC adsorption was used to pretreat electrospun fibers for mineralization with SBF solution enhancing the carboxylic acid content by an order of magnitude (Rodriguez et al 2011). Detailed micrographs showed the hydroxyapatite minerals nucleated from the fiber surface after modification with this anionic polymer. Additives do not always need to be polymeric to help induce mineralization on cellulose-based substrates. Rhee and Tanaka (2000) added citric acid to SBF solutions to nucleate hydroxyapatite growth on the surface of cellulose cloth.

The drawback of biomineralization is the slow kinetics of the process, which decreases the ability of mineralized structures to be manufactured in a timely manner. Typically, it takes between 7 and 14 da to mineralize samples depending on the level of modification required. However, there are a number of different electrolyte solutions used for the mineralization process. Enhancing the concentration of ions intensifies the rate of mineralization; the different solutions are referred to in terms of the concentration of ions found in SBF (1.5×, 2×, 6×, etc). By enhancing concentrations of compounds in the fluid, mineralized scaffolds can be produced in 24-72 h. Hofman et al (2006) successfully used a double soak procedure to get substantial mineralization of woven lyocell (regenerated cellulose with 4% carboxylic acid content) after 3 da of treatment. However, the caveat is that higher levels of concentration may cause minerals to precipitate without the surfaces actually nucleating the growth.

Bone, a lightweight structural composite, illustrates two design principles that can be adapted for biobased composites arising from the microstructural architecture and the degree of mineralization. There are two types of bone, soft trabecular bone and hard cortical bone. Differences arise in the microstructure. Trabecular bone is highly cellular with porosity greater than 50%. Light yet stiff composite panels have demand in furniture markets, and efficiently designed hybrid biobased composites may have a future role in addressing this need while conserving total amount of fiber in a panel. Also, the cellular nature is important for composite materials because the thermal insulating properties change, providing a unique approach for the design of panel-based products for green building products. The other design principle is that the stiffness of bone is tuned with the degree of mineralization (analogous to the density/stiffness relationship of wood) (Currey 1979). Hence, as the composite becomes less cellular and more mineralized, the mechanical properties of the material increase. These principles would allow a hybrid biobased composite to be tuned for application by controlling the degree of mineralization. Being able to tune mechanical properties, along with density, provides the ability for enhanced product design.

FUNCTIONALITY THROUGH CONTROLLED STRUCTURES

The scales of a butterfly wing have brilliant colors without the use of chromatic dyes. The brilliant colors arise from the microstructure of the scales. In one sense, the wing scales are similar to a stack of ceramic roofing tiles; there is a defined repeating structure and spacing such that incoming light is reflected at different planes. The light reflected at different levels causes interference with other incoming light, providing the iridescent appearance. Based on the properties and spacing of the tiles, color is controlled across multiple wavelengths of visible light. Brilliant color without paint provides a powerful and stable way to create colored surfaces that will not erode with time because of
chemical changes to dyes. With this design principle, cellulose nanoparticles were used to create defined layers resulting in interference patterns with color (Cranston and Gray 2006). In the simplest method, a suspension of nanoparticles is spin-coated (a method of drop deposition on a rotating surface with centripetal forces spreading the suspension in an even layer), and concentration of the suspension is used to control the interference patterns. Based on film thickness, color is tuned by the deconstructive interference patterns of light reflected from the interfaces of the film/substrate and film/air. Another method is to dip-coat a surface using the LbL method described previously with an ultrathin iridescent film created on the surface and the color controlled by the number of layers (Wagberg et al. 2008). A third method uses solution casting of cellulose nanoparticles; during evaporation, the particles form a chiral nematic liquid crystalline suspension with stacking of layers of nanocrystals that have a certain rotation per layer within the suspension. Because the spacing of these layers impacts the overall chiral nematic pitch, additives can be used to control and tune pitch difference, providing the ability to tune color from the visible to the near IR regions. Shoppowitz et al. (2010) demonstrated that ordered nanoparticle gels can be locked into place using silicate glass precursors (TEOS) as additives followed by acidic cross-linking. After heating the samples higher than the thermal decomposition temperature of cellulose in the presence of oxygen, a mesoporous glass film is formed with iridescent color. The unique approach is that depending on the viewing angle, the films can change colors.

In addition to color, structure is also very important at the surface for wetting properties. Both the leaf of the lotus plant and the foot of the water strider insect have structured roughness that helps to trap air and prevent wetting of water (Bhushan 2009). The result is that a water droplet placed on a lotus leaf has a contact angle >150° with very little hysteresis after rewetting. A contact angle of this magnitude causes a water droplet to appear as a sphere sitting on the surface. Commercial paint systems are available to make surfaces with these attributes, and this subject is one of the most developed areas of biomimicry. Clearly, this area of research is appropriate for wood and fiber science because water has a large-scale impact on durability of wood products and many materials are used in outdoor exposure. A recent development is freeze-dried nanocellulose particles sprayed (air-brushed) on surfaces and then chemically modified with fluorne chemistries (Mertanen et al. 2012). During the process, nanocellulose agglomerates into submicron particles with an appropriate surface roughness and the hydroxyl functionality allows facile modification with fluorne compounds to render the surface superhydrophobic. Another method using cellulose fibers is oxygen plasma etching of paper, which creates a surface with inherent roughness by selective removal of accessible areas. Sequentially, a fluorne plasma is used to treat the remaining cellulose at the surface, which results in a contact angle on paper that is >160° (Fig 5) (Balu et al. 2008). This method of modification allows for bulk material modification as a roll-to-roll process. Li et al. (2008) treated filter paper and cotton fabric with a potassium methyl silicate creating superhydrophobic surfaces based on the time of immersion. The resulting polymethylsilsesquioxane coating is a fluorne-free alternative method for creating hydrophobic surfaces.

**FUTURE OUTLOOK**

Organisms in nature rely on polymers and polymer–mineral hybrids to create a wide variety of properties from a few elements. Mechanical
performance and function were developed from controlled structure and architecture within the material. Because natural materials impart a broad range of useful functionalities for the organism, there are still a variety of design principles for manufactured materials that can be further developed to enhance performance while decreasing energy consumption and mitigating environmental impact during fabrication and disposal. For example, the antifouling structure of shark skin can be used as a bacterial-resistant surface without the use of biocides, and the adhesive-free bonding system of the gecko foot would make pressure-sensitive adhesives obsolete, making recycling of “stickies” easier. Stronger wet-spun cellulose fibers from aqueous solutions with better matrix–fiber interfaces would allow development of biobased-reinforced composites for structural applications, and further development of hybrid polymer–ceramic composites through biomimetic processes would decrease the energy consumption required for many current ceramics.

New developments in manufacturing paradigms for biomimetic materials are required because self-assembly and biomineralization occur in batch processes across extended periods of time. However, the overall design principle of controlled structure will probably continue to be the key element that drives innovation in sustainable biomaterials manufacturing in the near future. Coupling design principles to new manufacturing methods, such as 3-D printing or microreactor systems, may provide routes to incorporate timed processes and assembly into biobased composites with functional architectures.

ACKNOWLEDGMENTS

This work was supported in part by the U.S. Department of Agriculture NIFA NRI competitive grants program (Grant Number 2010-65504-20429).

REFERENCES


