

Manufacturing Processes for Advanced Materials: Nanocomposites

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Key words: thin film, functional coating, surface energy, plasma-enhanced chemical vapor deposition, nanoparticle, nanocomposite

Nanocomposite Manufacturing Technology – An Area of Critical National Need

Nanotechnology entails the manipulation of matter on an atomic and molecular scale. Considered high risk with the potential for high reward, nanotechnology generally involves structures on the scale of 100 nanometers or smaller. The field is very diverse, ranging from novel extensions of conventional device physics to completely new materials based upon molecular self-assembly. Nanocomposites, polymeric resins blended with nanoparticle fillers, are emerging as a promising new class of advanced materials. Mechanical, thermal, and electrical properties of these materials are expected to be far superior to those of conventional composites. However, a lack of efficient manufacturing capability currently prevents the widespread use of nanocomposite materials. In order for nanocomposites to become truly pervasive, their processing techniques must be improved to the point where production costs are more closely aligned with those in the chemical industry. Chemical processing is a strength of the US economy generating over \$689 billion a year in products [i]. Nanocomposite technology offers many potential benefits to the nation, but these will remain only as possibilities unless economical production methods are developed. Support is needed for research and development of large scale manufacturing to enable the efficient production of these advanced materials.

One major effort addressing funding of nanotechnology research is the National Nanotechnology Initiative (NNI), started in 2001. Since that time, the United States has invested approximately \$10 billion in infrastructure and research and development. The recommendation of the National Nanotechnology Advisory Panel (NNAP) for the NNI in 2008 was to commend and encourage investment in infrastructure and instrumentation in order to keep the US competitive [ii]. The NNAP reported evidence of “evolutionary changes impacting the market in a variety of materials and consumer products, including textiles, food packaging, home improvement tools and materials, sporting goods, reformulated drugs, and automobile parts. Ongoing research and development advances promise forthcoming revolutionary changes in energy capture and storage, molecular electronics, environmental sensing and remediation, and personalized medicine” (p. 10).

Background and Explanation of the Problem or Opportunity

The benefits and applications of nanocomposite technologies have multiplied in recent years. Almost every industry has been or could be revolutionized by developments in the field of nanocomposites, but few industries have adopted the technology. To understand why, one must consider the differences between industries with prevalent nanocomposite applications and those without.

Fields that currently utilize nanocomposite technology include medicine, electronics, sports equipment, and aerospace. These industries all enjoy a relative price insensitivity, but also face demanding technical challenges that justify funding of research for nanocomposite production. Medicine uses nanocomposite technology to deliver drugs, enhance diagnostic procedures, and interact with biological systems at the individual cellular level. Electronics and sports equipment industries utilize nanocomposites to generate performance edges that can lead to profitable new products, even through minimal improvements. Aerospace justifies the funding of cutting edge technology because of the extreme mission requirements and the ability to offset acquisition costs with long-term operational savings. All of these fields are early adopters of nanocomposite technology; a trickle down effect to more price sensitive

sectors is expected to occur as improvements are made over current production methods.

Material costs associated with nanocomposites are somewhat higher than those of conventional composite systems. However, the largest impediment to widespread adoption of nanocomposite technology is the lack of adequate processing methods. Although partially embraced by the specialized, high margin industries described above, most manufacturing enterprises have yet to adopt nanocomposite technology as they are already heavily vested in existing infrastructure and methods. For example, bridges and water works are infrastructure areas that could benefit from new nanocomposite applications to prevent corrosion and lessen maintenance costs. However, the initial financial burden of current nanocomposite technology is considered too great. The housing and building trades could enjoy new levels of profitability brought by innovations in fire retardancy and energy efficiency, as well as increased strength-to-weight ratios, but virtually no nanocomposite products have been integrated into standard building practices. The shipping industry could reduce fuel expense with nanocomposite hull coatings and agriculture companies could reduce the annual tonnage of chemicals with nanocomposites products if the price points were attractive.

In order for nanocomposite innovations to be fostered by new sectors of the economy, the cost/benefit ratio must be skewed in favor of traditional industries. This could be accomplished by two differing approaches: development of new nanocomposite production processes (i.e., engineering design of new tools and equipment for processing existing nanoparticles), or modification of currently available nanocomposite materials to allow for processing by established technologies. In this paper, AeonClad will advocate for the latter approach.

Enabling Nanocomposite Production through Surface Chemistry

Nanoparticles are defined by their miniscule dimensions which, when incorporated into composite materials, impart novel properties not present in the host matrix. Reactions at the surface of nanoparticles are the key to their unique functionality, as surface to volume ratios are extremely high for these materials. The performance of composite materials is largely governed by how intimately the filler material interacts with the surrounding polymer matrix; nanocomposites are no different in this regard. Unfortunately, the high surface area of nanoparticles leads to significant agglomeration that is difficult to overcome with traditional composite processing methods. The addition of surfactants to composite materials significantly increases particle dispersion, but also diminishes material properties.

Thin film coatings on nanoparticles themselves could be used to improve dispersion into polymeric matrices. If functionally reactive, these coatings could further be used to covalently bond the nanoparticles into the polymer matrix. For example, such a technology could be used to coat carbon nanotubes with a functional thin film that would allow for rapid dispersion and bonding into plastics (carbon nanotubes have yet to live up to their potential due to dispersion problems).

Unfortunately, the ability to efficiently coat nanoparticles is limited with current technology. Traditional coating and encapsulation approaches tend to fail at the nanometer scale. Liquid based coatings are the most mature approach, but suffer from processing problems including the inability to fully wet nanoscale surfaces, large volumes of wastes, and rather crude control of process chemistries and film thicknesses. Other approaches including self-assembled monolayers and sputtering have been used, but only offer limited flexibility in the properties of deposited films.

The ideal nanoparticle surface modification technique would have several features. It would be agnostic as to the size and shape of the particles to be coated. It would not require line of site for complete particle encapsulation, and it would allow for tight control the film thickness and porosity. Additionally, the coating properties (composition, chemical functionality, robustness etc.) would be tunable to a high degree. Ideally, all the process byproducts would be minimal and any waste material would be benign or easily disposed of.

Gas phase deposition processes are capable of meeting all the above requirements. Chemical vapor deposition has been applied to powders, and plasma enhanced CVD (PECVD) allows for creation of a wide variety of film chemistries.

PECVD has been used to create robust, pinhole-free, and conformal nanometric thin films on a wide variety of surfaces including metals, ceramics, plastics, powders, porous materials, nanoparticles and micropowders [iii]. PECVD is a single step coating process that uses no solvents and generates very little waste. These advantages have made PECVD an increasingly popular choice for coating or modification of substrates in numerous applications from the medical device and pharmaceutical industries to personal care and packaging. Proctor and Gamble has developed a commercial PECVD coating technology for use in their powdered detergent manufacturing processes to help with particle agglomeration and dissolution [iv]. Additionally, Ball Corporation coats 12,000 plastic wine and beer bottles an hour using a PECVD process to improve the taste and shelf life of beverages stored in these containers [v]. A large number of PECVD technologies have been utilized by a variety of medical and pharmaceutical companies including Novartis, Bausch and Lomb, and others. Applications in these industries include enhanced biocompatibility of implanted devices and contact lenses, as well as improvement of drug delivery [vi, vii, viii].

The PECVD process deposits polymeric thin film coatings made from a wide variety of compounds ranging from the monomers traditionally used in polymer science to less conventional materials that cannot be used in solution-phase polymerization. Many PECVD process parameters (power, coating time, monomer flow rate, and chamber pressure) can be adjusted to optimize coating properties. The variability in these parameters, as well as the wide range of compounds for deposition allows for a broader spectrum of potential surface modifications and coatings than can be achieved with traditional wet chemistry techniques.

Conventional PE-CVD processes operate in what is referred to as continuous wave (CW) mode; the RF power is on and the plasma is ignited for the entirety of the processing time. Due to the energetic nature of the process, specific film chemistries can be difficult to achieve. Additionally, film thicknesses are hard to control as both ablation and deposition occur simultaneously under CW conditions. In recent years, some advances in control of coating chemistry have been reported [ix, x, xi, xii, xiii, xiv, xv, xvi, xvii]. However, problems and limitations are still frequently encountered when attempting to utilize these approaches for synthesis of specific polymeric films. In particular, it is often observed that problems with film quality and adhesion are encountered when reaction parameters are varied too aggressively [xviii, xix, xx, xxi].

Pulsed-PECVD, a technique in which the plasma is rapidly turned on and off during processing, is not hindered by the limitations of CW PECVD processes. Pulsing the plasma increases control of film chemistry both by lowering the overall average process power, and by allowing molecules and ions to react via lower energy pathways during the plasma off times. The major benefit of this approach is that polymeric films with

specific organic functionality can be deposited onto substrates with a high degree of control. Both the type and the quantity of organic functionality can be controlled by this technique. For example, an array of films containing 0 – 13% surface carboxylic acid have been prepared by pulsed-PECVD of acrylic acid. Additionally, the lack of film ablation in this process leads to a linear increase of film thickness over time.

Pulsed-PECVD is an excellent candidate technology for nanoparticle encapsulation. If carried out on a commercial scale, the availability of non-agglomerating, functionalized nanoparticles would allow for significant improvements in nanocomposite manufacturing. However, much like other high risk, high reward emerging technologies, funding for commercialization has yet to be realized.

If funding for development of nanocomposite manufacturing processes was available, the technology would be leveraged for success across multiple sectors. Nearly every major industry including civil/construction, energy, water, manufacturing, aerospace, and medicine can expect to benefit from the successful commercialization of this technology. For example, both heavy industry and aerospace would benefit from new lightweight materials and improved corrosion resistance. Electronics and plastics would have new functionalities at reduced cost and environmental impact. Construction trades and building owners would enjoy reduced labor requirements and higher energy efficiency.

Funding Would Meet a Timely Need Not Met by Others

To date, funding for nanocomposite technology beyond basic research has been difficult to obtain. One hurdle for funding projects in this area is the complexity of the disparate fields needed to fully appreciate the technology and possible solutions. Both at the federal and investor level, cross-cutting expertise is needed to evaluate the potential risks and benefits of the technology. That semiconductor equipment can be used to lay down unique chemistry for a novel material to be used in a civil engineering or biomedical application is more than most agencies or venture capital groups care to understand. It is likely that either the technology or the potential applications will be outside of the expertise of any one particular group of investors or government agency.

Because of the diversity of the nanocomposite technology platform and governmental agency's priorities, there is an assumption that basic research and development is still needed, and few funds are provided for advanced technology scale up. Some agency examples include:

- National Science Foundation supports over 40 nanotechnology centers and only four of those are focused on manufacturing; only 5.5% of its 2009 NNI budget of \$397.2 million will go to manufacturing
- Department of Energy supports five nanotechnology centers; manufacturing is budgeted only 1.5% of \$336.9 million
- Department of Defense supports three nanotechnology centers; manufacturing is budgeted only 5.5% of \$464.1 million
- National Aeronautics and Space Administration supports four nanotechnology centers; no manufacturing has been budgeted
- National Institutes of Health supports 21 nanotechnology centers; manufacturing budget is only 0.2% of \$311.3 million [xxii, xxiii]

Of the \$1.66 billion NNI budget for 2009, only 3.9% is allocated to manufacturing. This is likely due to both reviewers for basic science who are not familiar with the

applications, and application driven agencies that are not familiar with the science. It is precisely because the platform is so broad and far reaching that funding has been difficult to obtain. Benefits are both substantial and broadly applicable to almost every industry, but achieving the requisite funding for commercialization efforts remains elusive.

Funding for development of commercial scale nanocomposite manufacturing processes has also been difficult to obtain from the private sector. Most industries have clearly defined criteria around which major companies and investors choose to compete (e.g., higher performance in the electronics industry or price in the commodities sectors). A new technology that does not fit into the existing paradigm stands little chance of attracting capital in this risk averse, short term survival climate. The science is complex and draws on multiple disciplines; the benefits are real, but diffuse across multiple industries. Most companies pay homage to innovation, however, few are willing to bare the burden of development costs without a guarantee of an exclusive market advantage. A clear path to patent exclusivity can be elusive as the prior art is dense. This leads to a large desire for technology that would enable new products, but no single company acting as a leader to fund the requisite technology development. Compounding this dilemma is the large number of market niches, each willing to be a customer, but no single niche being substantial enough to justify a considerable investment.

An often unspoken issue regarding nanotechnology in general is the assumption of poor scalability and commercialization. Use of nanoparticles and nanocomposites is still largely seen as an academic exercise with no real-world practicality. Reinforcing this bias is a lack of everyday products that incorporate nanocomposite materials.

Additional challenges of nanotechnology commercialization, according to the NNI, include a lack of standards, questions about environmental health and safety implications, limited/restricted venture capital, and insufficient education and workforce preparation [xxiv]. "Limited dissemination of knowledge/skill/expertise in nanotechnology is a continuing barrier to commercialization of the cutting-edge ideas that come out of the lab. The importance of the government role in educating scientists and engineers through investment in research and development cannot be overemphasized" (p. 24).

Nanocomposites Deliver the Potential for Impacts and Transformations

The implications of nanocomposite technology are extremely wide ranging. For example, use of nanocomposites can lead to innovations that allow surgeons to successfully repair a weakened artery, or allow agricultural scientists to develop more effective crop treatments. Ultimately, development of nanocomposite technology can lead to advanced materials, devices, and applications that improve life, health, safety, and the environment. However, the technology will remain on small, narrowly defined scales as long as funding continues to promote the limited focus of individual governmental agencies or companies seeking specific products. Supporting manufacturing infrastructure for programs that not only advance the technology, but offer scalable and cost efficient applications is necessary for nanocomposite technology to begin to reach its potential.

Customers for nanocomposite applications are generally interested in answers to three questions: does it work, will it scale, and what will it cost. Therefore, the deliverables for any effort in this area should enable mass customization across a broad platform of nanocomposite materials to address the question of "workability". A model plant to handle 250 pounds an hour would be sufficient to demonstrate a one million pound per

year capacity and show that the process can be commercialized. Economic assumptions can be validated at this scale as equipment, maintenance, and operating costs should be apparent and best operating practices established.

Success Would Provide Dramatic Benefits to the Nation

National economic benefits will flow from innovative processing technologies that are applicable to all classes of nanocomposite materials and can scale to the point of being so pervasive that they are taken for granted. Manufacturing of these advanced materials would build on the nation's strength in the chemical industry while also providing a viable opportunity for displaced workers in high tech industries such as semiconductor manufacturing. Nanocomposite technology is one of the future fields of materials science. It will allow more value to be inserted into products thereby increasing both customer utility and worker productivity, and directly improving the standard of living for all involved.

Lastly, the option of declining to pursue nanocomposite technology is not tenable in the current international climate. Foreign competitors are already advancing the state of the art. Major peer reviewed papers have recently come from research groups in France and South Korea, and researchers in the UK and China have also published in this field. To date, the European Union has more publications and China's output is also increasing [xxv]. Building on existing infrastructures and capabilities to leverage new opportunities is imperative for the long-term competitiveness of any economy. The United States must adapt its strengths for new challenges and utilize all its advantages for maximum effect. This white paper lays out just such a plan.

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