Scientific Review
ISSN(e): 2412-2599, ISSN(p): 2413-8835
Vol. 6, Issue. 6, pp: 41-47, 2020
URL: https://arpgweb.com/journal/journal/10
DOI: https://doi.org/10.32861/sr.66.41.47

Academic Research Publishing Group

Original Research **Open Access**

Bio Inspired Self-Curing Composite: A Leap into Augmented Enactment

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Article History
Received: May 7, 2020
Revised: June 2, 2020
Accepted: June 8, 2020
Published: June 10, 2020

Abstract

Relentless progress has been made on composite materials, their manufacturing processes and their structural design in past few decades. Nevertheless, the approval of composite materials in all engineering disciplines is constrained due to its susceptibility to various kinds of defects during manufacturing stage viz porosity, foreign body inclusion, incorrect fiber volume, bonding defect, fiber misalignment, ply misalignment, incorrect curing cycle, wavy fiber, ply cracking, delamination, fiber microstructural defects etc. Hence there was a requirement of techniques to somehow overcome these defects during the service life of composites being used in various structures and equipment. This promising field of research has made great progress over the past several years, but many procedural encounters are still to be overcome, and there exists a great need for focused research to address several areas of concern. On the other hand, nature has materials that have curing potential and repair strategies ensuring their survival. Sustained development in the field will produce new curing chemistries that possess greater stability, faster kinetics. Tailor-made placement of curing agents is dynamic research subject at the cutting edge of self-curing. New bio-imitative curing agents are closely connected to vascular networks. The purpose of this technical paper is to sort the methodology in line with ongoing research efforts in composites. A perspective on current and future self-curing approaches using this biomimetic technique is offered.

Keywords: Bio- imitative; Bio- stimulated; Self-curing Composites; Material science.

1. Introduction

Material mutilation, catastrophe are natural magnitudes of the modern day use. Thus the need for continuous enhancement of material is very necessary for today's engineering endeavors. So far, the concentration has been towards refining material by mechanical means. However, Self-curing materials introduce biological means to improve material property. A vital attention in existing scientific research is the improvement of bio stimulated material system. Nature's capability to heal has stimulated new concepts and new mechanisms in the engineering community.

Higher strength to weight ratio is one of the major reasons for increased demand of composites. In addition, they offer immense scope for integrating multi functionality due to their categorized grain structure. The approval of composite materials in all engineering disciplines is constrained due to its susceptibility to various kinds of defects during manufacturing stage viz porosity, foreign body inclusion, incorrect fiber volume, bonding defect, fiber misalignment, ply misalignment, incorrect curing cycle, wavy fiber, ply cracking, delamination, fiber microstructural defects etc. Another limiting factor in their wider exploitation is relatively poor performance under impact loading, a critical aspect of any vehicle design, leading to a significant reduction in strength, stiffness and stability [1, 2].

The perception of self-curing composites comes from the ability of human beings to heal mutilated cells by using inherent chemicals/resources available to them. Hence the self-curing material proposes a new path for longer lasting components and obviates the catastrophic failures. The curing potential of human beings provides the lead to various researches for self-curing composites: A leap into augmented material behaviour. The proficiency of curing is therefore regulated by the balance of rate of damage versus rate of curing.

2. Strategems for Self Curing

Nature's ability to heal has stimulated new philosophies. Different curing concepts have been projected that are capable to re-establish the mechanical enactment of the material. Exciting prospect is the combining of the futile surfaces. One area of interest is the fusion of the failed surfaces. Polymeric materials possessing selective cross-links between polymer chains that can be broken under load and then reformed by heat have been shown to offer healing efficiencies of 57% of the original fracture load [3]. Another example is where a polymeric material hosts a second solid-state polymer phase that migrates to the damage site under the action of heat [4, 5]. Hayes, *et al.* [5] have developed a two-phase, solid-state repairable polymer by mixing a thermoplastic healing agent into a thermosetting epoxy matrix to produce a homogeneous matrix which contrasts with the discrete particles of uncured epoxy reported by Zako and Takano [4].

Although not explicitly stated by the authors, [Lee *et al*, 2004] have considered the possibility of using nanoparticles dispersed in polymer films to deposit at a damage site in a similar fashion to blood clotting. Later work by Gupta, *et al.* [6], using fluorescent nanoparticles, has shown that ligands on the nanoparticles can be selected to help drive nanoparticles into a crack in a microelectronic thin film layer. The third area of interest is based upon a biological 'bleeding' approach to repair, i.e. microcapsules and hollow fibres. Microencapsulation self-curing [7-9] involves the use of a monomer, dicyclopentadiene (DCPD), stored in urea-formaldehyde microcapsules dispersed within a polymer matrix. Self-curing materials can be classified broadly into three groups: capsule based, vascular, and intrinsic [10].

The use of hollow glass fibres embedded in a composite laminate was pioneered by Bleay, *et al.* [11]. The ability to 'see' and become aware of internal damage in composite materials is as critical as in the human body. The ability to form a 'bruise' within a hollow fiber self-curing composite material was investigated by Bond and Pang [12].

3. Bio Stimulated Self-Curing Approaches

There is an opportunity of using nanoparticles which are dispersed in reinforcement films to deposit at a damage site in a similar fashion to blood clotting. In this work, the nanoparticles are dispersed in reinforcement films within a multilayer composite. The mechanical properties of the composites refurbished in this manner could potentially achieve 75%–100% of the undamaged material strength. Later work by Gupta, *et al.* [6], using fluorescent nanoparticles, has shown that ligands on the nanoparticles can be selected to help drive nanoparticles into a crack in a microelectronic thin film layer. By using Fluorescent nanoparticles, it has shown that curing agents on the nanoparticles can be selected to help drive nanoparticles into a crack in a microelectronic thin film layer. No refurbishment of mechanical properties was investigated.

When we talk of self-curing method, biological 'bleeding' approach comes into picture for repair, i.e. microcapsules and hollow fibres. Microencapsulation self-curing includes the use of a monomer.

When the microcapsules are burst by a progressing crack as shown in Fig 1, the monomer is drained along the fracture where it comes into interaction with a dispersed particulate catalyst initiating polymerization and thus repairs. similar to the arteries in a natural system, has been investigated at different length scales in different engineering materials by various authors, for example, in bulk concrete [13, 14], in bulk polymers [13], and in polymeric composites.

Fig-1. Ruptured Capsule

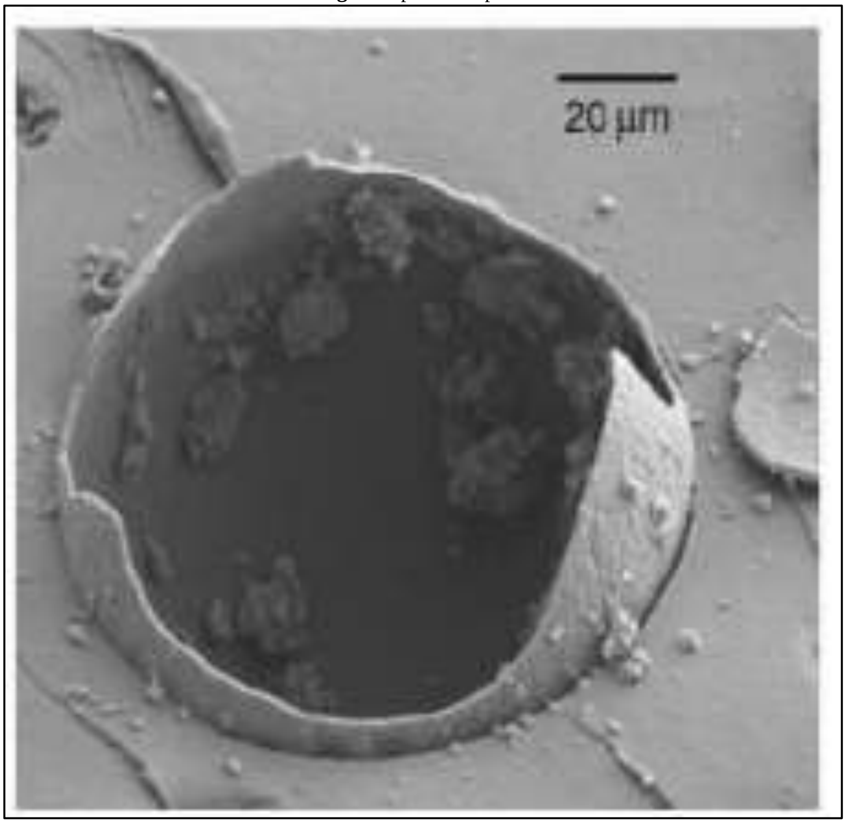
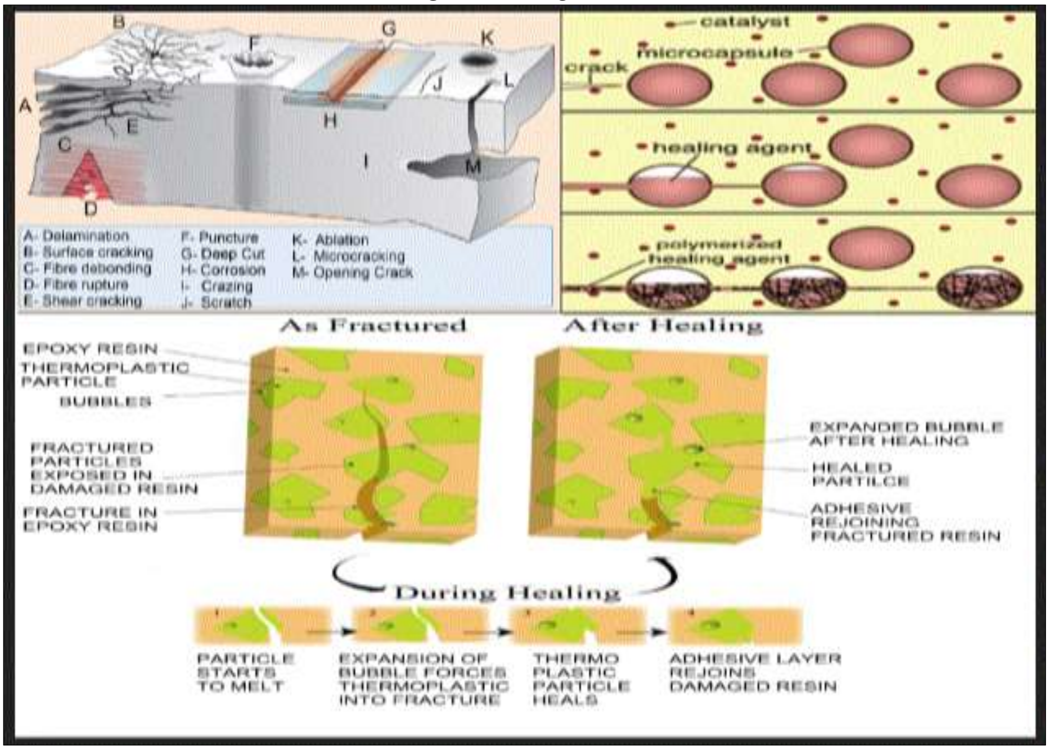


Fig-2. Self-Curing Process



at a millimeter length scale [15] and at a micrometer length scale – see Figure 2 [11, 12]. The release of active components was clearly seen to restore a proportion of the loss in mechanical properties arising from micro cracking within a polymer matrix. When a polymeric material hosts a second solid-state polymer, there is a phase that drifts to the damage site under the action of heat. A homogenous matrix is harvested by mixing a thermoplastic curing agent into a thermosetting epoxy matrix. These systems offer the capacity for self-curing.

Benefit of microencapsulation self-curing approach is the simplicity with which they can be merged within a bulk reinforcement material. The disadvantages are the need for microcapsule rupture and the need for the resin to meet the catalyst prior to any repair taking place. In fibre reinforced composite material, additional problems arise due to the size of microcapsules (typically 10-100μm) disrupting the fibre construction, the need for a good dispersion of the catalyst to provide uniform curing functionality, microcapsules having only partial resin volume, and the creation of a void in the wake of the crack after consumption of curing resin. Some results Kessler et al, 2003 [8] have indicated specific problems in terms of healing efficiency due to clumping of microcapsules into woven-roving wells whilst cracks propagate along woven-roving peaks.

The crucial engineering challenge is to appreciate and extract basics of natural systems so that to produce systems that can feasibly and cost-effectively be applied to various engineering structures. Accelerated environmental testing of self-curing systems is critically needed. While the massive research on self-curing in retort to rupture has focused on quasi-static performance, the ultimate utility of self-curing systems is in contesting with fatigue and/or periodic damage events.

Moderately miniature research has been dedicated to the dynamic aspects of self-curing under fatigue like conditions. Self-curing reinforcement could extend the concept of self-curing beyond the repair of matrix dominated failure modes. Self-curing designs will most likely depend on particular distribution of curing agents in large-scale applications to improve efficiency while reducing the cost and detrimental effects to the matrix material.

Epoxy-based systems have received the most attention in self-curing quasi-static Mode I fracture experiments. The first successful autonomic self-curing in a thermoset epoxy resin was by White, *et al.* [7], demonstrating 75% recovery of virgin fracture toughness of TDCB (Tapered Double Cantilever Beam) specimens with a DCPD-Grubbs' catalyst capsule-based healing system. The tapered geometry of the TDCB specimen, was the first basic structure introduced [16] to study self-healing Thermo setting Polymers.

The method of curing employs hollow fibres fixed within an engineering structure, similar to the arteries in a natural system, it has been studied that at different length scales in different engineering materials, commercial hollow fibres were consolidated into lamina and then manufactured into composite laminates, i.e. the self-curing material acts as the structural fibres. The significant advantage of the hollow fibre self-curing concept is that the fibres can be positioned to match the alignment of the neighbouring reinforcing fibres thereby reducing Poisson ratio effects.

The fibres can be placed at any site within the piling order to address specific failure threats. Different curing resins can be used reliant upon the working requirements of the structure. Similarly a different instigation methods can also be used to cure the resin and crucially a significant volume of curing agent can be made available. The drawbacks are the relatively large diameter of the fibres when compared to the reinforcement, the necessity for fibre fracture, the need for low viscidness resin systems to facilitate fibre and damage infusion and the need for an additional treating stage for fibre infusion. The ability to identify and become aware of internal damage in composite materials is as important as in the human body.

4. Bio-Imitative Self-Curing Approaches

The diversity in bio-stimulated approaches in composite materials has been already discussed in previous section. Till few years back, different self-curing approaches were being considered and assessed from an engineering perspective. Recently the studies have begun into underlying biological methods, mechanisms and procedures in order to provide a truly bio-imitative self-curing solution. The challenge for the future is the evolution of ‘engineering self-curing’ near a bio-imitative elucidation. To date, this work is still in its beginning.

A proposed measure of self-curing under fatigue loading is the fatigue life extension (λ) defined in terms of fatigue life (N) by Brown, *et al.* [17]

$$\lambda = \frac{NCURED - NCONTROL}{NCONTROL}$$

The capsule-based self-curing system demonstrated a fatigue life extension of $\lambda = 2$ for a tensile Mode I fatigue test incorporating a single unloaded thermal rest period of 120◦C for 10 min after a 12.5% reduction in stiffness. Curing efficiencies (as defined in above equation) [10] on the basis of recovery of compressive strength (σ) as

$$\eta CAI = \frac{\sigma CURE - \sigma DAMAGED}{\sigma VIRGIN - \sigma DAMAGED}$$

The independent curing materials in engineering structures have been distributed arbitrarily all over the structure or spaced regularly through the composite laminate structure. In nature the system is personalized for a specific meaning with the curative medium often being multifunctional. The first reported instance of adapting the location of self-curing functionality in engineering to match the destruction hazard is by Trask and Bond. In this work the fundamental failure interfaces were recognized and then the hollow fibre self-curing system was designed for a specific composite element and operational environment, in this case a space environment. The equation for that is represented as:

$$\sigma_{xx} = \frac{E}{1-\nu^2}\left[\frac{\partial u}{\partial x} + \nu\frac{\partial v}{\partial y} - z\left(\frac{\partial^2 w}{\partial x^2} + \nu\frac{\partial^2 w}{\partial y^2}\right)\right] - \frac{E}{1-\nu}\alpha\Delta T$$

$$\sigma_{yy} = \frac{E}{1-\nu^2}\left[\frac{\partial v}{\partial y} + \nu\frac{\partial u}{\partial x} - z\left(\frac{\partial^2 w}{\partial y^2} + \nu\frac{\partial^2 w}{\partial x^2}\right)\right] - \frac{E}{1-\nu}\alpha\Delta T$$

$$\sigma_{xy} = G\varepsilon_{xy} = \frac{E}{2(1+\nu)}\left[\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x} - 2z\frac{\partial^2 w}{\partial x \partial y}\right]$$

The need for self-curing in the space environment was found to put significant demands on the restoration means in terms of mechanical properties, process ability and environmental compatibility. The self-curing mechanism was found to refurbish 100% of the strength when equated to undamaged laminates containing curing plies. Verberg, *et al.* [18], have computationally studied a biomimetic “leukocyte” consisting of microencapsulated nanoparticles that are released by diffusion while the microcapsule is driven along micro vascular channels.

The work which is carried out till now has been Bio stimulated and not bio-imitative, although this is gradually transforming. The meaning of bio-imitative self-curing utilised in this work is that some methodical study of biological curing methodologies must be used to power the approach adopted. Clearly, the period for realisation of self-curing inside engineered structures will be significantly abridged by a comprehensive assessment and study of the many instances of how the natural world commences the process. Bio mimicry of the multifaceted integrated microstructures and micro mechanisms institute in biological organisms offers significant scope for the development in the design of future multifunctional materials. It is suggested that above the yield point, load sharing between the yielded thread and the other threads permits recovery by a reversible cross-linking mechanism [19, 20].

In composite materials the customary engineering approach is to project the reinforcing fibres with the same strain to failure response. Perhaps a better damage tolerance strategy would be to implement an amalgam composite material that mimics the safety policies observed in living creatures. This method, although not exactly self-curing, would permit the expansion of composite materials with elastic-plastic behaviour. This methodology could be taken one step further, if the yielded fibres, and maybe the matrix material, could then be ‘healed’ to recuperate its novel stiffness. A composite with the capability to improve from transient overload in the principal loading direction could be developed. This would upgrade a significant disadvantage of composite materials. The healing potential of fractured bone in the human body is influenced by a variety of biochemical, biomechanical, cellular hormonal and pathological mechanisms [21]. In a homogenization method to create an effective elastic-plastic polymer reinforced matrix, the composite behaviour can be modelled by linearization of the local behaviour through the use of the tangent or secant stiffness tensors of the phases. The differential equation of equilibrium for an infinitesimal element of a composite in terms of stresses are given below. These stresses needs to remain balanced even after self-curing to ensure stability of the composite in use.

$$\frac{\partial \sigma_{xx}}{\partial x}+\frac{\partial \sigma_{yx}}{\partial y}+\frac{\partial \sigma_{zx}}{\partial z}+X=0$$

$$\frac{\partial \sigma_{xy}}{\partial x}+\frac{\partial \sigma_{yy}}{\partial y}+\frac{\partial \sigma_{zy}}{\partial z}+Y=0$$

$$\frac{\partial \sigma_{xz}}{\partial x}+\frac{\partial \sigma_{yz}}{\partial y}+\frac{\partial \sigma_{zz}}{\partial z}+Z=0$$

where X-, Y- and Z- are body forces per unit volume.

A list of effective self- healing agents discovered till date is presented below at Table 1. There are other agents which are being experimented for their feasibility but are yet to be documented.

Table-1. List of self-curing agents

Material	Healing approach	Chemistry/method	Healing measure	Max. Eff.	Ref.(s)
Epoxy/epoxy sphere phase/glass FRC	Capsule based	Meltable epoxy spheres	Peak fracture load	100	Zako and Takano [4]
Mendomer 401/carbon FRC	Intrinsic	DA-rDA reaction	Strain energy	94	Park JS, Kim HS *et al.*
2MEP4F polymer	Intrinsic	DA-rDA reaction	Fracture toughness	83	Xiangxu, *et al.* [3]
Epoxy/thermoplastic phase	Intrinsic	Meltable secondary additive	Fracture toughness	77	Hayes, *et al.* [5].
2M4F polymer	Intrinsic	DA-rDA reaction	Fracture toughness	57	Xiangxu, *et al.* [3]
Epoxy vinyl ester	Capsule based	PDMS-tin catalyst	Fracture toughness	24	Cho *et al.*
Mendomer 401/carbon FRC	Intrinsic	DA-rDA reaction	Strain energy	94	Plaisted and Nemat-Nasser [22]

5. The Leap

Self-curing in fibre reinforced composite materials has been predominantly directed on the potential offered by the polymer matrices because typical impact impairment is broadly dependent on the medium. However, the strengthening stage develops majority of the strength and stiffness within any composite material, and it is these integral properties those would benefit meaningfully from a self-curing ability and dwindle other failure modes.

The curing potential of fissured bone in the human body is subjective by a variety of biochemical, biomechanical, cellular hormonal and pathological mechanisms. The curative procedure is a persistent state of bone deposition, desorption, and remodelling. The regular procedure of bone curing is a complex procedure including blood clotting, development of collagen fibres, mineralization (stiffening) and transformation of the collagen matrix into bone. This preliminary 'woven' bone, which can be reflected as arbitrarily organized collagen bundles, is remodelled and substituted by mature 'lamellar' bone. The remodelling procedure can take up to 18 months to complete in which the curing bone is restored to its novel shape, edifice and mechanical strength. This course can be enhanced by the application of an axial load to the fracture site. This loading helps the formation of bone to align with the key load path and the rearrangement of bone where it is not required. The remodeling process can take up to 18 months to complete in which the healing bone is restored to its original shape, structure and mechanical strength [21]. This process can be accelerated through the application of an axial load to the fracture site. This loading promotes the formation of bone to align with the primary load path and the redistribution of bone where it is not required [21].

The restoration of fissured synthetic strengthening fibres has yet to be undertaken in an engineering framework. Likewise, the in-situ development of supplementary fibres to backing added project loads, similar to branch growing in trees has not been considered. The difficulty with this method is the span compulsory for growth, which are dubious to be realistic for engineering applications.

Self-curing concepts may lead to improved utility. Longer life, safer self-curing batteries, resealing tires, fade-resistant fabrics, and anti-tamper electronics are all potential applications for self-curing concepts. Yet what lies beyond curing? Biological systems again provide a road map for potential research paths. Many critically important biological materials, for example, bone, regenerate and remodel. In the future, synthetic materials that currently heal in response to damage may one day respond in a more regulated fashion so that regeneration and remodeling occur over the lifetime of the material in response to mechanical loading. The system is also reconfigurable in response to circumstances by adjusting the radius of individual vessels by vasoconstriction and dilation in mature tissue, or by growth in embryonic blood vessels [23].

Mammalian blood clotting has evolved around the chemical reactions of a series of active enzymes and their inactive precursors known as clotting factors. The intrinsic system takes the form of an enzyme "cascade" or "waterfall" of reactions involving clotting factors. It was first proposed by Macfarlane Macfarlane [24] and Davie and Ratnoff [25]. Nature also offers alternative healing strategies to the repair of brittle materials, such as the use of materials that regain strength after yielding. For example, mussel byssal thread is capable of regaining strength after yielding [19, 20] whilst lection in abalone [Smith *et al*, 1999] possesses microstructures that are broken during loading and reformed during relaxation. In distal byssal threads an initial modulus of 600MPa with a yield point occurring between 20-30% extensions was reported by Vaccaro, *et al.* [20].

6. Concluding Remarks

The escalation of composite designers towards self-curing leads to lesser mass structures with increased service life. Self-curing methods especially for the composites have predominantly been bio stimulated. The detailed study of natural curing to allow true bio-imitative self-curing is the latest development. New bio-imitative curing agents are closely connected to vascular networks. Compartmentalization is a substitute strategy that bridges the gap between self-curing and the more traditional engineering damage tolerance design philosophy and particularly appropriate to the problem of moisture ingress into damaged composite structures. Post-curing reclamation may offer a self-curing approach for overloading in principal loading direction, which would be vital step in of direction self-curing technology, though the behavior of self-curing material under environmental exposure is still a major topic of discussion.

For this purpose, the current engineering world doesn't have supporting model. Foreseeing the endurance of self-curing composite, it is currently beyond the capability of available analytical tools to predict the life cycle. However, accelerated efforts are required to switch laboratory demonstrations into successful and practical applications across a broader cross section of industries. Present approaches to self-curing can be applied to other material properties. Properties such as conductivity may be restored for utilization in the microelectronics industry, in which the existing key is typically chip replacement. Conductive curing agents also show potential for restoring electrical conductivity using Capsule-based or vascular approaches. Balazs and coworkers have both modeled and experimentally observed nanoparticle segregation to material defects, which may be applied to conductive particles in conductive substrates.

Up till now Nature has been found to be the best teacher even for engineers and researchers. Bio mimicking is not a new concept but the challenge remains in absolute understanding of the bio engineering fundamentals to obtain desired result.

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