Beyond the limits of material performance

Nanobase resin systems & films, innovative epoxy formulation

NANOLEDGE

A new vision of value creation in high performance materials.

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INTRODUCTION

During the last decades, improvement in processes and better control of raw materials have enabled composite designers and manufacturers to access a variety of new markets by enabling innovative products or innovative product features. Introduction and use of composite materials in transportation, aerospace, sporting goods, civil engineering, military applications and wind energy is a testimony of the huge economic and technical value of these new materials.

Nevertheless, there is a need to improve performance of the current composite materials to move forward in existing applications and further penetrate new markets.

To all players in the industry, it is obvious that further development of composite materials will highly depend on innovative solutions to get:

1. Better performance enabling the design of lighter parts and structures, ensuring durability of materials, and making composites multifunctional;
2. Green materials (namely use of natural fibers and bio based resin systems) and clean technologies (for example those that reduce the use of solvents) to answer the growing demand of the market.

What are the solutions to manufacture tomorrow's materials?

As obvious as it may appear, it is important not to consider composites as merely the sum of several components but rather as a synergy of these components. Formulation of composites is as much an "art" as it is science; the performance of a composite is dependent on the "smart" combination of the right ingredients.

After an introduction on the composite industry context and related definitions, this document will cover the main limits currently experienced by composites. This will serve as the basis for a highlight of the potential solutions in terms of mechanical, electrical and thermal properties of composites.

CONTEXT

In the last thirty years, composite industry growth made these materials cost-effective and competitive in terms of performance (Figure 1) to address a large number of applications and enable access to numerous markets.

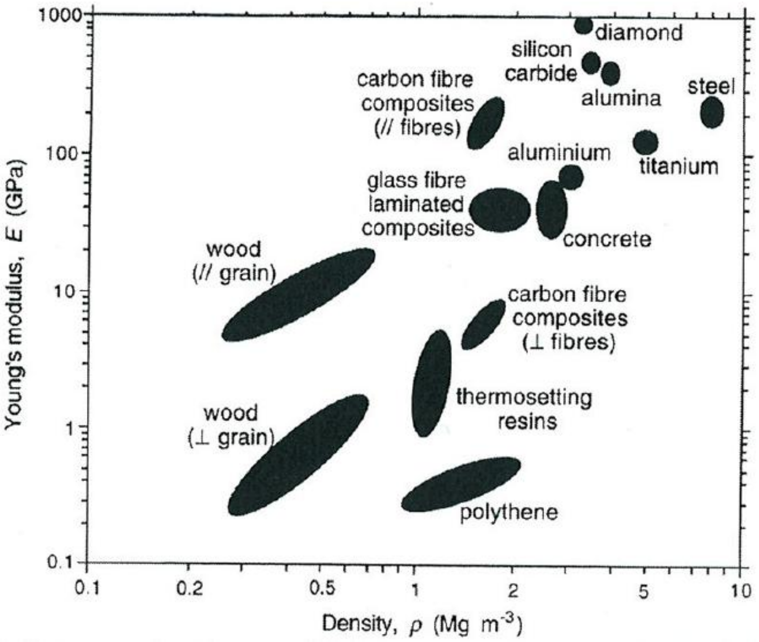


Figure 1: Data of some engineering materials; Young's modulus vs. density

Aerospace is a good illustration of the use of composite materials in which they replaced metallic parts. For instance, airframes of new generation civilian aircraft (e.g. Boeing Dreamliner, Airbus A350) are 50% made of composite materials, as measured by weight. This enables drastic weight reduction and leads to huge fuel savings.

Wind energy is also representative of what can be achieved using composite materials.

Today, wind blades more than 60 meters long are being routinely manufactured
(see Figure 2).

Only composites have the high performance / weight ratios that are required to enable the construction and operation of such structures.

Figure 2: Wind turbine exhibiting rotor blade length of 126 meters

Nevertheless, manufacturers have reached the limit of what they can deliver using current composite material. It is worth noting that these restrictions mainly arise from the properties and performance of the underlying raw materials which in turn determine the design and manufacturing limits.

These limits need to be overcome if manufacturers are going to:

- Design larger composite parts and resulting structures,
- Reduce weight of the composite parts, and
- Increase substitution of materials such as metal to avoid weight, corrosion or costs issues.

To do so requires better (multi-functional) raw materials. Multi-functionality is fast becoming a key point for the composite industry.

For instance, an ideal material for an aircraft frame will combine high stiffness, elasticity, flexibility, impact resistance, and sufficient conductivity to dissipate electrostatic loads and even a lightning strike.

In conclusion, a real technical breakthrough is expected and required for raw materials if composite's share of manufactured goods is to continue to rise.

DEFINITION & LIMITS

1 – About Composites

Composites are combinations of at least two different materials showing significantly different physical and chemical properties. The resulting material has better properties than each of the components alone. Commonly, a composite material is made of a reinforcement (fibers or particles) and a binder (matrix resin system).

Whereas the reinforcement ensures strength and stiffness of composites, the role of the matrix is to:

- Bind fibers,
- Transfer mechanical stresses,
- Protect fibers,
- Provide chemical resistance, and
- Define the shape of materials.

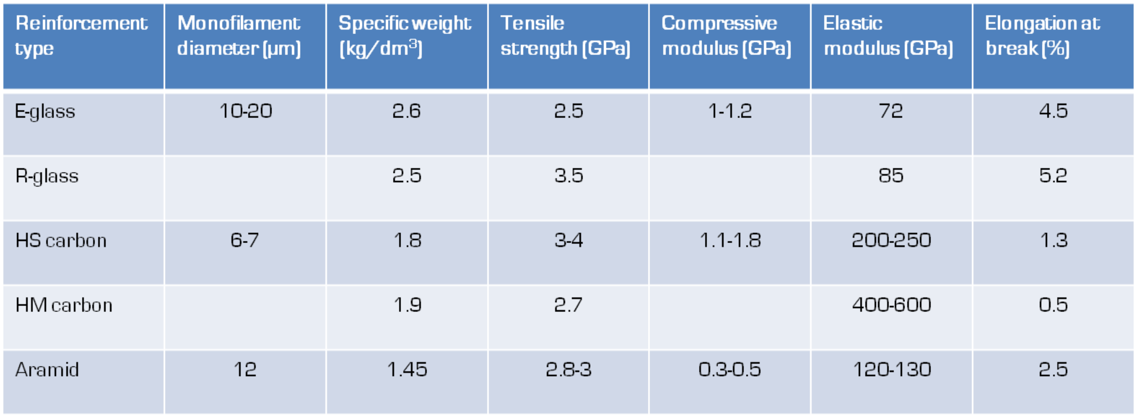
At the most abstract level, considering only raw materials, the general properties of composites will depend on:

- Fiber
- Matrix
- Fiber/ Matrix Interface

2- Reinforcing fibers

Focusing on High Performance (HP) composites, Nanoledge's chosen sector, means that only continuous fibers will be discussed.
Typical properties of the most common reinforcing fibers are summarized in Table 1.

Table 1: Typical properties of reinforcing fibers



Reinforcement type	Monofilament diameter (µm)	Specific weight (kg/dm³)	Tensile strength (GPa)	Compressive modulus (GPa)	Elastic modulus (GPa)	Elongation at break (%)
E-glass	10-20	2.6	2.5	1-1.2	72	4.5
R-glass		2.5	3.5		85	5.2
HS carbon	6-7	1.8	3-4	1.1-1.8	200-250	1.3
HM carbon		1.9	2.7		400-600	0.5
Aramid	12	1.45	2.8-3	0.3-0.5	120-130	2.5

An overview of carbon fiber and aramid fibers properties – mostly used in HP composite – are given in respectively Table 2 and Table 3.

Table 2: Qualitative characteristics of carbon fibers[1]

Advantages	***Drawbacks***
- Mechanical properties (tensile strength, compressive strength, modulus) - Temperature resistance up to 2 000°C (except in oxidizing atmosphere) - No longitudinal thermal expansion - Non magnetic and X-ray permeability - Electrical conductivity - Moisture resistance - Machinable - Specific weight (1.8)	- High cost - Chemical behavior in oxidizing atmosphere and in the presence of metal (galvanic corrosion) - Low impact and abrasion resistance - Poor adhesion to resins

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[1] M.Reyne. *Composite solutions thermosets and thermoplastics.* JEC publication, 2006

Table 3: Qualitative characteristics of aramid fibers[1]

Advantages	***Drawbacks***
- Specific tensile strength - Low specific weight (1.45) - No thermal expansion - Damping properties - Impact and fatigue resistance - Hydrocarbon resistance	- High cost - Low compression strength - Moisture absorption - Poor adhesion to resins - UV sensitive - Low fire resistance, decomposition at 400°C - Low machinability

3- Matrix: Epoxy systems

While Nanoledge has skills and knowledge that could be applied to a number of matrix types, the company has chosen to focus on epoxy systems as matrices. Epoxy resins represent a large share of the high performance market among other reasons because they offer the right balance between performance and processability.

For example, in comparison with unsaturated polyesters or vinyl esters, epoxy resins have better:

- adhesive properties (ability to bond to the reinforcement or the core),
- mechanical resistance (namely stiffness),
- resistance to fatigue and micro cracking,
- thermal resistance: from 80 to 250°C,
- chemical resistance to water, acids and solvents.

Epoxy systems are used in various processes such as wet lay-up, Resin transfer Molding (RTM), infusion, filament winding, pultrusion, preimpregnation or resin film infusion (RFI).

As for any formulated "balanced" system, epoxy systems imply some compromises:

- Systems must be fully adapted to the planned manufacturing process, sometimes at the cost of some performance; the same formulation/system cannot be used for pultrusion and wet layup without some adaptation;
- Systems are a fragile equilibrium: increase in one of the desired properties may impact another one. For instance, most often, increasing flexibility will decrease stiffness,

- Some useful components are or will be covered in the near future by more and more stringent regulations. Environmental impact is rapidly becoming a key and growing constraint in the set-up of formulations.

4- Fiber/matrix interface

From a mechanical point of view, efficiency of the combination between fabric and matrix depends on the transmission of stresses from the composite as a whole to the fibers that provide the composite with the desired strength, *i.e.* it depends on the fiber / matrix interface quality. Interface quality is mainly related to:

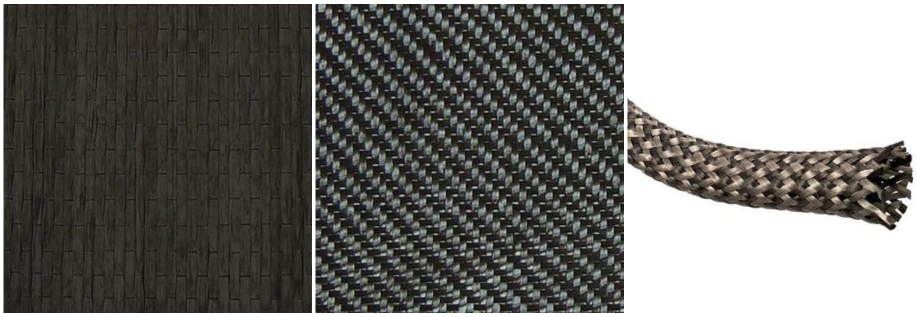
  - Fiber surface chemical composition and ability of the matrix to chemically bond to the fiber;
  - Fiber roughness: the rougher the fiber, the higher the contact surface, the stronger the bond;
  - Fiber size and shape;
  - Matrix viscosity: optimal viscosity is required to impregnate fibers, to the matrix must be liquid enough to "penetrate" the fiber filaments and remain within the fibers while still being workable for the manufacturing process;
  - Shrinkage during curing: if shrinkage of the matrix is too different from the shrinkage of the fibers, internal stresses will appear at the interface, weakening the composite from day 1;
  - Presence and nature of any impurities in the matrix or within the fibrous material; impurities tend to induce stress concentrations, making the composite weaker at these points;
  - Ageing.

5- Reinforcing architecture & design

Due to long fiber orientation, a composite structure is anisotropic (i.e. which has properties that differ according to direction). The fiber reinforcement is strong in the fiber direction. Consequently, the structure will be optimized by judiciously positioning the reinforcement structure or fabric in the direction of the stress. This sometimes may be subtle when solicitations arise from various directions and namely not in the fiber orientation (for example, the bottom bracket of a bicycle frame has to resist to compression and flexural stresses oriented in several directions). When stresses are multi-directional, multiple fiber layers with different orientations are often used.

Given a set of constraints, a designer will select amongst the following reinforcement approaches:

- Unidirectional (UD): UD fabrics/tapes (Figure 3-a),
- Multidirectional oriented: 2D or 3D fabric (Figure 3-b),
- Braid (Figure 3-c),
- Multiple layers of the above



a b c

Figure 3: Main reinforcement morphologies

Multidirectional fabrics limit the anisotropic behavior and provide high impact resistance due to better cohesion between fibers. On the other hand, some stresses and frictions are applied on the fibers during weaving which decreases tensile and flexural properties of the final part.

Unidirectional fabrics or tapes are the best solution with respect to reinforcement. They enable designers to efficiently place the fibers according to known load orientation on a part but require a deep understanding of the nature and orientation of the various forces and stresses on the part being designed). Layer orientation can be calculated thanks to theoretical models, finite element analysis and software programs (Figure 4).

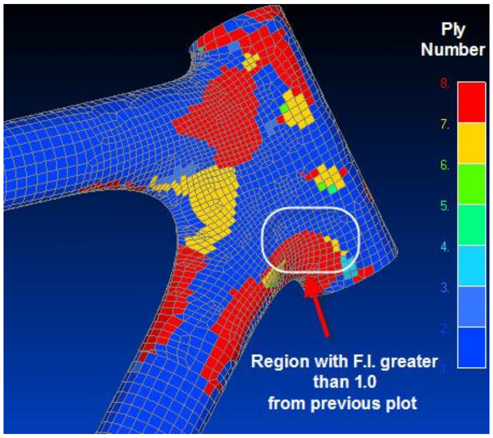


Figure 4: Bike frame finite element analysis simulation

An example of optimized design is to use UD fabrics or tapes on the internal layers to ensure tensile and flexural strength and bi directional fabric on the outer layer to ensure durability of the part.

6- *Processes*

Mechanical properties of composites will depend on the selected process. Process selection has a large impact on the resin content by weight, molding ease and resulting defect content (e.g. air bubbles, impurities) of the composite part.

Main processes for high performance composite manufacturing are:

- Infusion
- Autoclave moulding
- RTM (resin transfer moulding)
- Pultrusion
- RFI (resin film infusion)

Each process requires specific properties in terms of matrix viscosity and curing cycle. Autoclave moulding using prepregs and resin film infusion produce excellent balance between properties and thickness (weight) since they lead to low resin content (20 to 35%) but are relatively expensive to set up. Nonetheless, parts size limitation, equipment costs and production yield often lead manufacturers to select a different process.

7- Limits of composite materials compared to metallic structures

Metallic structures are versatile systems and have been used for a long time (in terms of performance and processing). Their main limitations are weight and oxidation. Composites help on both fronts. However, to obtain lighter structures thanks to composites, designers face several limitations.

- Temperature resistance & fire resistance

For epoxies, the highest temperature resistance of the resulting composites is between 200 and 250°C which represents an important limitation for some applications. There are other organic matrices that enable higher temperature resistance but still far from metallic structures.

Fire resistance is mandatory for aerospace and transportation applications. Even if some matrices comply with current norms, it is obvious that a more performing additive would enable formulators to develop more versatile systems (namely with less compromise on other parameters such as processability).

- Sudden failures

Composite are brittle and their failure is not accurately predictable.

Three failure mechanisms exist for composites (Figure 5):

  - Delamination occurs if the interface between fibers and matrix is weaker than needed or if the resin content is too high.
  - Transverse crack results from a bad penetration of the resin system between the filaments of the fibers during the manufacturing.
  - Fiber break is explained by a non uniform transfer of loads from the matrix to the fiber or, of course, by fiber defects.

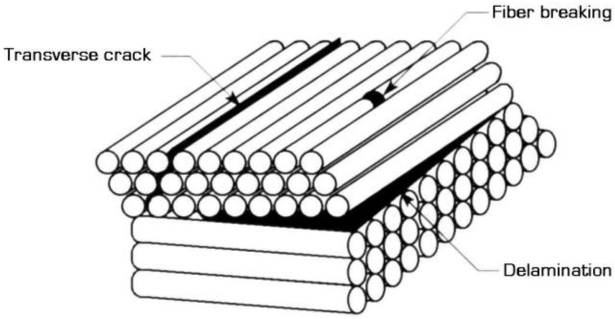


Figure 5: Composite failure mechanisms

- Conductivity (thermal & electrical)

For some aerospace applications, electrical conductivity is required. Conductivity of composites is generally low compared to metallic structures. Up to now, the best alternative has been to incorporate a metallic mesh within the composite structure. A lighter solution such as an intrinsically conductive composite would be ideal.

- Fatigue resistance / Impact resistance

Thanks to high elasticity modulus, metals resist well to cyclic loading. On the other hand, composite materials offer very high stiffness combined with a low toughness which can be detrimental to their impact resistance and to their durability when subjected to cyclic loads.

- Compression resistance

Low compression resistance is generally a significant drawback of composites and results in their delamination: fibers exhibit impressive tensile behavior but confer very poor compression resistance. Consequently, any compression resistance exhibited by a composite mainly arises from the properties of the matrix itself. As such, it is well known that current matrix performances limit designers' choices of product architectures.

INDUSTRIAL SOLUTIONS

Ranging from raw materials to composite manufacturing, several avenues of improvement are either available or being developed.

1. Fiber improvement

Bonding capacity can be improved either by chemical treatment or by physical modification.

The chemical appraoch consists in applying an additive to the filaments that contains binding, coupling and anti-static agent which results in increased wettability of the fiber by the matrix. Besides guaranteeing the matrix/reinforcement bonding capacity, the additive makes it possible to bind the filaments together to make a yarn, and stops cracks from propagating in case of fiber breaking. It also lubricates the fibers to protect the yarn from abrasion due to friction between fibers during the weaving process, and from corrosion during use.

The physical approach consists in grafting nanoparticles onto the fibers. Thanks to their extremely low size and important aspect ratio, nanoparticles increase the active surface of the resulting fibers thereby improving the strength of the matrix to fiber bond (Figure 6).

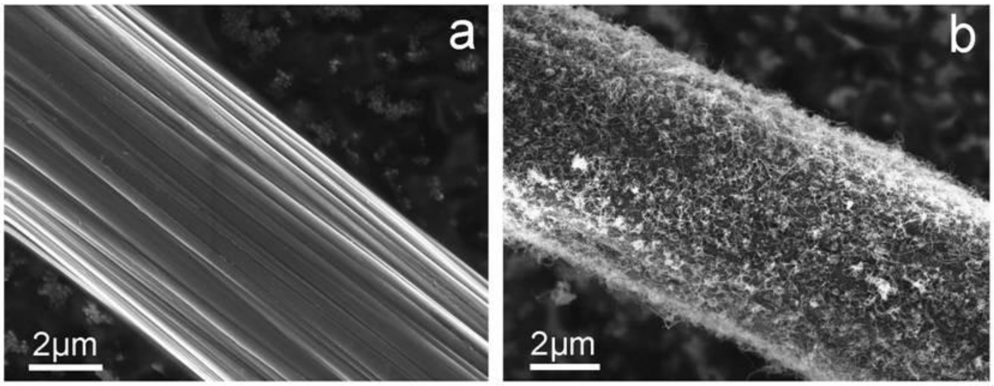


Figure 6: SEM observation of a) carbon fiber and b) carbon fiber grafted with CNTs by CVD

In addition, some nanoparticles have tubular shapes which enable improved anchorage of the matrix. Until Nanoledge, this strategy has been evaluated at the lab scale but not available yet at the industrial scale.

2. *Resin system enhancement*

Matrix is essential to get the required composite cohesion and to overcome the brittleness of some fibers. Some part manufacturers focus on fiber selection and do not realize that performance is also due to the matrix. Whereas some formulators work on traditional chemistry to make traditional formulations, innovative companies such as Nanoledge have oriented their research on nanochemicals and green additives and their interactions with the fibers in the composites.

2.1. Nanoparticles overview

Thanks to their excellent intrinsic properties, nanoparticles are the best innovative solutions to boost performance. After several years of studies and industrial projects, Nanoledge has a perfectly integrated dispersion solution and the knowledge required to control several nanoparticle types such as: graphitic, metallic and silica nanoparticles, auto associative nanoparticles and nanoclays. The aim is to integrate those nanoparticles into epoxy systems to address the various known limitations of composites such as fatigue resistance, impact resistance, fire resistance, compression resistance, etc. Nanoparticles are a performance enabler; they improve particular properties without negatively affecting the other overall performance of the composite materials.

The key to achieving these dramatic performance boosts is in the dispersion and separation of the nanoparticles into the resin. In some cases, further gains can be achieved by chemically bonding the nanoparticles to the resin. Note that when nanoparticles are not well dispersed, they can even cause defects in the resin system.

To benefit from nanoparticles, the formulation step is very important. Adding nanochemicals tends to increase viscosity rendering the resulting mix difficult to use without manufacturing process modifications. As a result the overall resin formulation needs to be adapted to fit with process requirements: That is called Nanoformulation.

From the environmental point of view, resin-bound nanochemicals are non toxic, non pollutant and their filling ratio is really low; typically in the range of 0.1% to 5% of the total formulation depending on the nanoparticles used.

The variety of available nanoparticles provides for a broad range of new performances and even for multi-functionality of composites.

2.2. Nano Improvements

2.2.1. Damage tolerance improvement

As discussed previously, damage tolerance is a real limitation for replacing metallic structures by composite materials. Nanoparticles, when properly used, have been shown to increase crack initiation and crack propagation resistance. For instance rubbery nanoparticles such as auto associative nanoparticles or core shells are able to absorb a fraction of the internal stresses thereby significantly delaying crack initiation. The flexural properties of composites are also slightly increased by those kinds of particles.

Similarly strong nanoparticles, such as carbon nanotubes or nanoclays improve the crack propagation resistance. Cracks are stopped and reoriented in various directions to release the internal stresses. Instead of a big crack which could lead to sudden failure, lots of micro cracks in the matrix enable the composite to keep its integrity.

Both of these mechanisms have a significant effect on impact resistance and fatigue resistance. Thousands of tests performed by Nanoledge and its clients have shown an impact resistance increase of the order of 30% and load-reload cycles increased by a factor of 2 before breaking. For instance hockey sticks using these nano-enhanced resins better support impact and have a longer life than traditional designs.

2.2.2. Compression resistance

A similar mechanism to the one just described allows carbon nanotube enhanced systems to improve compression resistance by around 20% compared to traditional systems.

2.2.3. Temperature resistance, flame retardant & fire resistance

Thanks to their structrure, bulky nanoparticles are able to increase the Tg of composites and their heat distortion temperature.

Nanoclays are used to enhance mechanical performance but also bring temperature performance benefits. Thanks to barrier properties provided by nanoclays, resin systems flame resistance is increased as illustrated in figure 7. The fire retardant mechanism stems from a reduction in the rate at which oxygen can penetrate into the polymer which thereby decreases flammability.

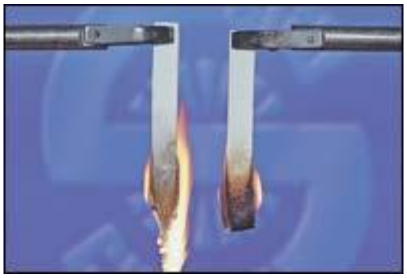


Figure 7: Flame retardant effect of nanoclays; On the left is the neat specimen, on the right the one with nanoclays

Degradation of a polymer by fire entails a chain reaction that creates so-called radicals which degrade the material. Nanoparticles act as traps for the radical thereby limiting the degradation propagation within the matrix.

2.2.4. Conductivity

Thermal and electrical conductivity of epoxy systems can be dramatically improved by adding a graphitic structure such as properly conditioned CNT or graphene platelets to the mix. These nanoparticles have very high intrinsic conductivity levels which contribute to increase the conductivity of the resulting composites. In contrast to most other improvement mechanisms where only modest loading results in significant changes to the composite's properties, conductivity improvement requires high filling ratio (between 1 and 5% of the total formulation) (Figure 8).

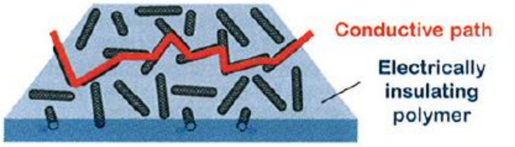


Figure 8: Conductivity mechanism using nanoparticles into resin systems

2.2.5. Nanoblending

Nanoblending consists of the judicious selection and conditioning of various nanoparticle types combined with the appropriate resin formulations in order to obtain a desired mix of enhanced properties. In Nanoledge's experience, the right choices have led to some synergistic effects between the various components that have in turn resulted in technical breakthroughs for several applications.

For example, Figure 5 shows the difference in the fracture toughness of the same epoxy formulation modified or not with nanochemicals: shown are the results for neat resin, CNT-enhanced and nanoblend-enhanced systems.

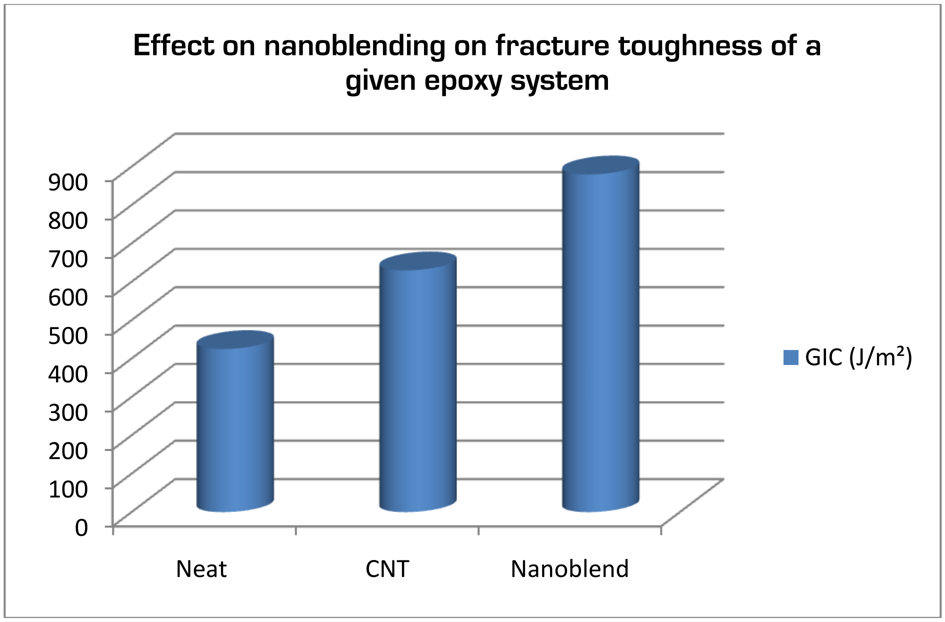


Figure 9: GIC values obtained for 8 layer carbon fabric composite made by RFI (resin film infusion)

Note that 0.3% CNTs in the system provides 50% improvement in fracture toughness compared to the neat resin whereas the nanoblend provides a 100% improvement. Once again, as in most Nanoledge formulated systems, other properties are only slightly or not affected.

Taking advantage of nanochemicals for enabling innovative performance of materials and getting environmentally friendly composites, this is Nanoformulation by Nanoledge.

3. *Processing solutions*

As shown previously, overall performance of composites results from the combination between materials, processes and technologies.

Consequently nanoformulations in and of themselves are not sufficient to deliver the desired results. For example, reproducibility of the results obtained thanks to nanochemicals will vary depending on the process used. Consequently Nanoledge has adapted its systems for the various processes used by its clients.

To make ensuring high quality and performance in composites parts easier to predict and achieve, Nanoledge has developed a nano-enhanced semi-solid resin film which could be processed by RFI or prepregging (Figure 10).

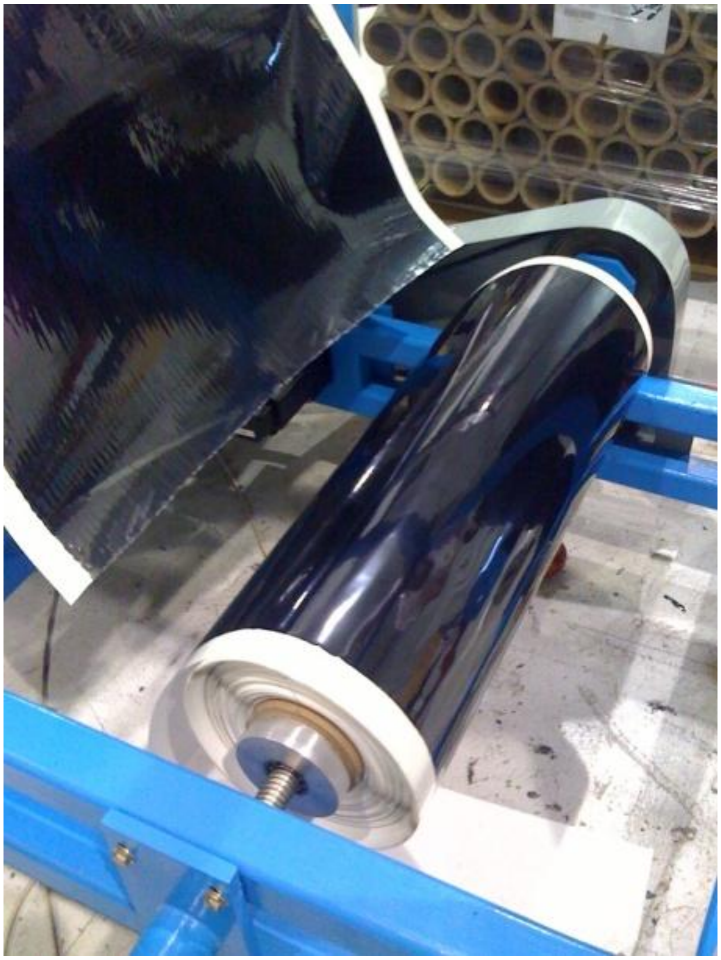


Figure 10: Nanoledge semi solid nanofilm stacked onto 3k carbon fabric

The film form factor provides several benefits:

- Direct access to innovative performance without the need for customized formulations,
- Reproducibility; it limits the potential for human error and for defects and makes the manufacturing process easy to set up and execute,
- Safe handling for part manufacturers,
- Environmental compliance (no solvents).

The Nano enhanced resin film is the best industrial and cleanest technology currently available to radically and simply improve performance, durability and processability of high performance composite materials.

CONCLUSION

Performance of composites depends on raw materials, design, process and process parameters, and above all on the synergy of those parameters.

Up until now, the strategy was to obtain the best compromise between all these factors to achieve the targeted performance. Nanoledge has developed a unique expertise in the innovative chemistry and nanochemistry required to improve matrix performance with a focus on processability. Nanoledge's technology ensures this performance improvement translates into performance not only of the raw materials but also in performance for the final composite-made product.

Development of nanotechnologies in the field of composites makes it possible to exceed the current performance limitations in terms of both durability and multi-functionality. In addition, nanochemicals have the potential to help composites comply with environmental constraints thanks to the reduction in the use of traditional additives and solvents. It is worth noting that the extra cost of these greener solutions is widely compensated for by the additional performance.

Furthermore, Nanoledge's introduction of a new form factor for delivering nano-enhanced performance makes it possible for industrial players who do not have the in-house expertise in chemistry required to work with complex matrices, resins and formulations to bypass this step altogether and simply use the film to get these performances.

Taking advantage of nanochemicals for enabling innovative performance of materials and getting environmentally friendly composites, this is **Nanoformulation** by Nanoledge.

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