Polymer-Clay Nano-composite materials for Thermal/Radiation shielding and Load Bearing Structural Applications in Aerospace/Defence

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Abstract

The paper provides a proposal for a pilot project aimed at the creation and use of Polymer Clay Nano-composites (PCN's) in the Aerospace/Defence and other industries. PCN's have been investigated and commercialized for use in multiple consumer and automotive applications. The use of PCN's may enable the creation of low-cost high-performance composite materials. Due to the conservative nature of the Aerospace/Defence industry, PCN's can potentially be good candidates for adoption and commercialization in relatively short term.

The paper proposes a simulation-driven approach to the creation of PCN candidates and their evaluation as nano-composite materials. A prototype project is proposed for work on PCN's with academic and industry partners. The development plan, timelines, licensing strategies and intellectual property are discussed. An assessment is made of the potential investors and the investment risk in the opportunity.

An introduction to the various technologies used in PCN's as well as a discussion of the some of the key issues is provided. The paper also presents an overview of the current composites technologies based on Fibre Reinforced Polymers and their usage in Aerospace and other industries. The underlying drivers that would facilitate the adoption of nano-composite materials are discussed. The characteristics of Aerospace and other industries are discussed to determine the criteria for selection of appropriate Micro and Nano Technologies (MNT's) for rapid adoption.

1. Rationale for Recommendation

Overview: The purpose of this paper is to provide a technological and programmatic background to the applications of Micro and Nano Technologies (MNT's) in the creation of thermal/radiation shielding and load bearing structural nano-composite materials for use in Aerospace and other industries.

A nano-composite material is a mixture of a conventional material with a nano-scale material. Nano-composite materials combine the bulk properties of conventional materials with the size-dependent properties of nano-scale materials to create composite materials with novel properties. The range of potential nano-composite materials is infinite.

The paper addresses one particular class of nano-composite materials, Polymer-Clay Nanocomposites (PCN's), which are created by adding clay particles to polymers. The paper argues that PCN's are a demonstrated MNT based platform that is ready for near-term commercialization and utilization (unlike many other MNT's). We believe that PCN's will enable novel low-cost nano-composites, with large market potential as evidenced by multiple commercial uses of PCN's.

Based on the current uses of PCN's, CANEUS has a unique opportunity to create a PCN based program focused on the needs of the Aerospace/Defense industries with benefits in other industries. The proposed Pilot Project will enable CANEUS to play a fundamental role in the creation of new nano-composites and to retain control over the generated IP.

Introduction: Structural materials are the materials that make up all the engineering structures in the world. The primary markets for structural materials are in Construction, Aerospace (civilian and military), Automotive, Bio-medical, and Consumer (e.g. sports equipment) industries. These industries are different in terms of their feature requirements, market drivers, product development cycles, cost structures and ability to take technology risks. The Aerospace industry is conservative, but pushes the envelope in looking for advanced materials with new features. The automotive industry is highly cost driven. The bio-medical industry is not cost-driven, but is conservative and has a limited materials knowledge base. The optical and electronic industries are innovative and have short product development cycles. Finally the consumer segment is innovative and willing to take technology risks, and has very short product development cycles.

People look at two main criteria when evaluating new materials: performance and cost. In terms of performance, people typically look for materials that are harder, tougher, stronger, stiffer or more elastic and more corrosion resistant. In addition, it is desirable to look at combinations of properties e.g. hardness and toughness, strength and low weight, toughness and transparency etc. In terms of cost, generally, the lower the cost the better. However, as briefly mentioned earlier, lower cost is not the primary driver for all industries. Figure 1 below shows the relative emphasis placed by each industry mentioned on cost and performance.
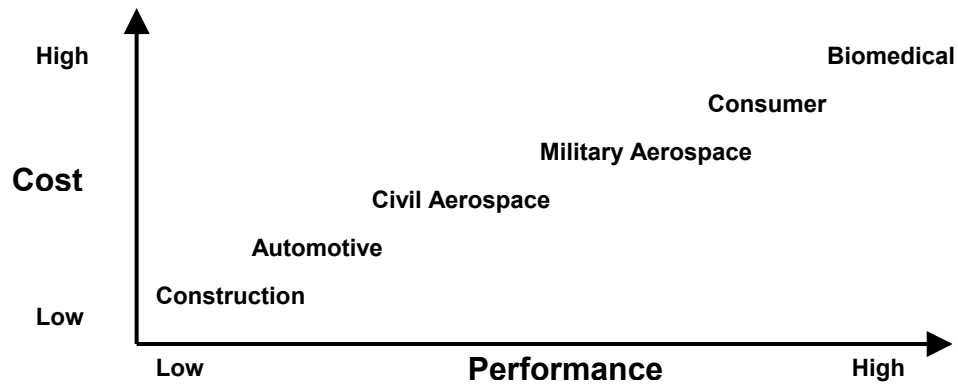
Figure 1: Relative importance on cost and performance in different industries.

It is fair to say that nano-composite materials would have to provide real performance advantages that people are willing to pay for. These advantages can manifest themselves in two ways: First, in an incremental fashion, and sometimes a little improvement is worth a lot, for example when it enables one to get past a performance or requirement barrier. Second, by enabling a new property that is not available any other way. For example, nano-materials could have new extreme properties (e.g. exceptional hardness or corrosion resistance), new combinations of properties (hardness and toughness) or unique processing capabilities (e.g. accurate near-net fabrication).

The requirements and the drivers of specific target industries will drive the future success of any prototype developed. Since the primary target is Aerospace/Defence, in this section, we will identify the various criteria important to Aerospace and use them to define the desirable characteristics of any candidate MNT that would be used for prototype development.

Important characteristics of the Aerospace/Defence industry: The Aerospace/Defence industry has a ubiquitous need for new materials for structural applications. However, the Aerospace/Defence industry has several unique features that impose important constraints on the kinds of technologies that can be considered relevant for the purpose of this paper.

The Aerospace industry can be broadly characterized by: (i) complex system level requirements, that lead to (ii) long development times and consequently to (iii) risk aversion. Performance issues, safety requirements and the need to conform to established standards drive complex system level requirements. As a result the development times can be very long, in some cases approaching a decade between technology development to flight incorporation. Because of complex system level requirements, the industry prefers to work in an evolutionary manner to successively reduce technology risk.

Characteristics of emerging MNT's: Many emerging MNT's carry a significant amount of technology risk. By and large, they are at an early stage of development and many of them are still laboratory concepts. In some cases there are basic science issues that need to be resolved. Since there is a considerable road to be traversed between a laboratory concept and a commercial version of a technology, it is not clear what exactly is the value proposition or benefit of the technology. Without a clear understanding of the benefits of MNT's, the commercialization path for many of these technologies is not currently defined and is only beginning in some cases. Since there have been no widespread successful commercial applications of MNT's to date, there is a dearth of experienced teams and entrepreneurs who have an established track record. These characteristics of MNT's do not resonate well with the requirements of the Aerospace industry, especially if one is looking for relatively near term commercial applications.

Criteria for selection of suitable MNT's: This forces us to consider only those MNT's that are relatively mature and whose applications have been initially demonstrated in some other industries that are less conservative and risk averse than Aerospace/Defence. We have to look at the possibility of building upon an established base of MNT's to deliver compelling and near-term commercializable technologies to the Aerospace/Defence industry. In addition, we have to look for a demonstrated value proposition in relevant market segments as well as the ability to move into new market segments.

2.   Current State-of-the-Art

Fibre Reinforced Polymer (FRP) composites: FRP's constitute the current state of the art for the use of composites in Aerospace/Defence. An FRP composite is a matrix of polymeric material that is reinforced by fibres or other reinforcing material. There are multiple constituents of FRP composites: Resins, Fibres, Fillers, Additives and Adhesives. Each of these ingredients plays an important role in the processing and performance of the end products.

Resins are polymers that are usually petrochemical or natural gas derivatives. Their primary function is to transfer stress between the reinforcing fibres and to protect them from mechanical and environmental damage. There are two broad categories of resins, Thermoset and Thermoplastic. Thermoset resins are liquids or low melting point solids that "cure" with heat, which is an irreversible process. Some examples of Thermoset polymers are Polyester, Vinyl resin, epoxy, Phenolic, and Polyurethane. These resins are known for their thermal stability, chemical resistance, reduced creep, reduced stress relaxation and low viscosity. Thermoplastic resins are solids that soften to viscous liquids when heated, and reversibly undergo the solid-liquid transition on heating or cooling. Some examples of Thermoplastic resins are Acetal, Acryronitrile butadiene styrene (ABS), Nylon, Polypropylene (PP) and Polyethylene terephthalate (PET). These resins are known for their rapid and low cost formation process, ability to reform and agreeable forming pressures and temperatures.

Fibres carry load along their length and provide strength and stiffness in one direction. They can be oriented to provide desirable strength and support properties in the directions of the primary loads. The fibres can be natural or man-made. Natural fibres include Cellulose and sisal. Man-made fibres include aramid, carbon/graphite, boron, glass, Nylon, Polyester, Polyethylene and Polypropylene. Glass is the most common fibre used in all applications, though carbon/graphite are the most common in Aerospace applications. Glass has high strength, high water corrosion resistance, good electric insulating properties and low stiffness. Aramid (Kevlar) has superior resistance to damage as an energy absorber, moderate stiffness and is good in tension applications like cables. Aramid is also more expensive than glass. Carbon has good modulus at high temperatures and excellent stiffness however it is brittle and has low electric insulating properties. Carbon is also more expensive than glass. The fibre reinforcements themselves can be done in multiple ways: roving, chopped strands, matte (chopped/continuous strand), woven roving, stitched, braided, unidirectional and veil.

Adhesives are primarily used to join different composites. There are many types: Acrylics, Epoxies, Urethanes, Phenolics and Silicones. The selection of particular adhesive is important given the use, however, the most critical part is the curing of the adhesive.

3.   Baseline Use

Overview of Industries: FRP's find extensive use in various industries. In the Construction industry strong growth is being seen in the creation of composites based structures and in the reinforcement of concrete structures. The slow deterioration of infrastructure is leading to increased opportunity for the use of new materials and structures. In the Consumer sector, growth is being driven by the use of composites in residential applications as well as in leisure goods like sports equipment. The Automotive industry is one of the largest markets for composites. There are different drivers for the automotive industry for US and Europe. In Europe there is a greater emphasis on recyclability and lower weight. In. the US the emphasis is on strength and performance. This has affected the choice of polymers used. In the US there has been a growth in Thermoset plastic usage whereas in Europe the emphasis has been on thermoplastics.

FRP Market Size: The 2001 global market for composite materials was 5.73 million tons or about $15 billion. The largest markets are US, Western Europe and Asia-Pacific with 31%, 27% and 26% of the global market share respectively [27,28].

Market (2001)	Size ($ Billion)	Shipments (M	CAGR (%)
W. Europe	$ 5.9	1.54	3.8
US	$ 7.1	1.78	2.8
Asia-Pacific	$5.6	1.45	6.2

Figure 2: Comparison of FRP market sizes for W. Europe, US and Asia-Pacific.

In all three markets, as summarized in Figure 3, Transportation (Automotive) applications are the single largest segment, with about 30% of consumption, followed by Construction and Consumer segments.

	k tonnes	%
Aerospace/Defence	11	1%
Industrial	152	9%
Construction	352	20%
Consumer	115	6%
Corrosion	201	11%
Electrical/Electronic	177	10%
Marine	192	11%
Transportation	576	32%
	1775	

	k tonnes	%
Aerospace/Defence	104	6.8%
Industrial	150	9.7%
Construction	324	21.0%
Consumer	157	10.2%
Corrosion	90	5.8%
Electrical/Electronic	150	9.7%
Marine	80	5.2%
Transportation	485	31.5%
	1540	

Figure 3: Comparison of FRP market segments for US (left) and W. Europe (right).

4.   Leading Aerospace Applications

Some 50 years ago, aircraft designers began taking advantage of the high strength-to-weight ratio associated with composites by replacing aluminum parts with others made from the newer materials. The design change helped reduce aircraft weight thereby increasing fuel efficiency. In addition to lower weight, composites were also attractive to engineers because their resistance to corrosion and fatigue compares with metals.

The types of composites and extent to which the materials have been used in aircraft have changed over the years. For example, a few percent of fiberglass, which is a glass fiber based resin as described above, was used in the 1950's in Boeing 707 passenger jets. By the 1960s, high-stiffness boron and graphite fibers embedded in epoxy resins became available, and the U.S. military focused on using these materials in rudders, ailerons, and other movable parts that control the motion of aircraft. Not long thereafter, boron fibers became widely used in the horizontal stabilizers of F-14 Tomcat fighter jets. And in today's F-22 fighters, carbon fiber composites and related materials compose nearly one-third of the jet's structure. Even greater reliance on composite materials is predicted for future military aircraft.

Figure 4: V-22 (Osprey) tilt rotor aircraft.

Some of the sophisticated capabilities of modern military aircraft wouldn't be possible without today's advanced composites. The *V-22 (Osprey)* tilt-rotor craft (Figure 4), for example, is able to take off, land, and hover like a helicopter, as well as reorient its rotors in midair and fly like a turboprop airplane. That kind of aeronautical capability is due in part to the graphite-fiberglass rotors and other lightweight composite-based structures in the rotor system that are strong enough to tolerate high centrifugal forces yet remain slightly flexible. Similarly, the extreme aerial maneuverability of F-18 fighter jets is partly due to composites used in the aircraft's wings, flaps, vertical and horizontal stabilizers, and other crucial parts.

Focusing on space applications, Cyanate based resins used in satellites because of toughness, resistance to micro-crack formation and radiation damage resistance.

5. Drivers for Change

Due to more demanding performance requirements, the trend in Aerospace/Defense is to use composites for more structural components in civil and military aircraft. While military aircraft are now using composites for primary airframe structures on aircraft such as the Joint Strike Fighter, the civil sector in Europe and the US is developing composite wings for next-generation aircraft. There is also a trend towards the manufacture of all-composite small civilian aircraft, either pressurized or un-pressurized, for executive and business travel. The US leads this with a number of small aircraft manufacturers currently going through certification.

These trends highlight the following needs within the Aerospace/Defense sectors:

1. There is a need for multi-functional materials, e.g. materials with superior structural and thermal properties, especially for use in high performance airplanes and spacecraft, for example. Multi-functional materials do not only reduce overall system weight, but also provide new set of properties to be utilized by aircraft and spacecraft designers.

2. There is a move towards lower cost materials and lower cost manufacturing processes such as resin transfer molding. This cost drive is evident in the potential broader uptake of composites within commercial aircraft in particular. Interestingly enough, weight alone is no longer the primary driver in this sector and the use of composites in new components such as wings depends on the ability to make the components at a cost competitive to the traditional material and manufacturing process. Figure 5 shows the cost of various materials in $/kg.
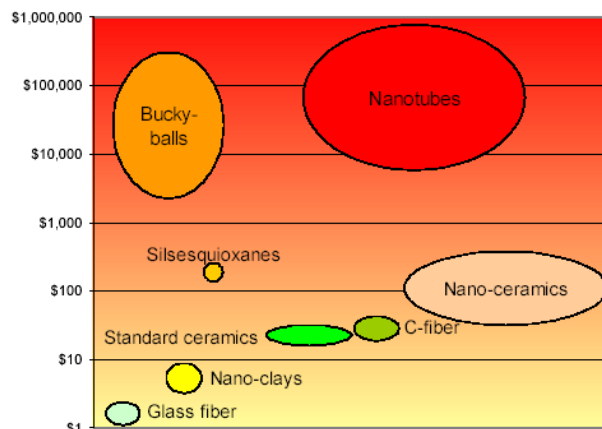

Figure 5: Cost of materials in $/kg.

3. In order to meet the requirements of Aerospace/Defense, there is a need for rapid development processes for the identification and creation of new nano-composites.

6. Polymeric Nano-composites

The reinforcement of polymers using fillers, whether inorganic or organic, is common in the production of modern plastics. Polymeric nanocomposites represent a radical new alternative to these conventional filled polymers or polymer blends. In contrast to conventional systems where the reinforcement is on the order of microns, Polymeric nanocomposites are exemplified by discrete constituents on the order of a few nanometers. Uniform dispersion of these nanoscopically-sized filler particles (or nano-elements) produces an ultra-large interfacial area per unit volume between the nano-element and host polymer. These dimensions also imply that the distance between nano-elements is comparable to their size.

This immense internal interfacial area and the nanoscopic dimensions between nano-elements fundamentally differentiate Polymeric nano-composites from traditional composites and filled plastics. These characteristics imply the overall performance of Polymeric nano-composites can not be understood by simple scaling arguments that begin with the behavior of traditional polymer composites. Thus new combinations of properties derived from the nanoscale structure of Polymeric nano-composites provide opportunities to circumvent traditional performance trade-offs associated with conventional reinforced plastics, epitomizing the promise of nano-engineered materials.

From both a commercial and military perspective, the value of Polymeric nanocomposites technology is not based solely on mechanical enhancements of the neat resin. Rather, its value comes from providing value-added properties not present in the neat resin, without sacrificing its inherent processibility and mechanical properties.

Traditionally, blend or composite attempts at 'multifunctional' materials require a trade-off between desired performance, mechanical properties, cost and processibility. The literature is full of examples that suggest Polymeric nanocomposites technology provides a route around these traditional limitations [1-6].

Considering the plurality of potential nano-elements, polymeric resins and applications, the field of Polymeric nanocomposites is immense. Development of multi-component materials, whether microscale or nanoscale, must simultaneously balance four interdependent areas: constituent-selection, fabrication, processing, and performance. For Polymeric nanocomposites, this is still in its infancy, and ultimately many perspectives will develop, dictated by the final application of the specific Polymeric nanocomposites.

7. Polymer-Clay Nano-composites

Overview: As defined earlier, Polymer nano-composites are a mixture of a conventional material with a nano-scale material. In the case of Polymer-Clay Nano-composites, the clay particles act as the nano-material. Nano-composite materials combine bulk properties of conventional materials with the size-dependent properties of nano-scale materials to create composite materials with novel properties. The range of potential nano-composite materials is infinite.

Clays or layered silicates (alternatively referred to as 2:1 layered aluminosilicates, phyllosilicates, and smectites) are the most commonly used inorganic nano-elements in Polymeric nano-composites research to-date. Layered silicates possess the same structural characteristics as the well-known minerals talc and mica and are comprised of hydrated aluminosilicate [10]. Their crystal structure and habit are summarized in Figure 5.

In the figure, the Van der Waals interlayer (or gallery) containing charge-compensating cations (M+) separates covalently bonded oxide layers, 0.96 nm thick, formed by fusing two silica tetrahedral sheets with an edge shared octahedral sheet of either alumina or magnesia. The charge per unit cell (generally between 0.5 and 1.3) originates from isomorphous substitution within the silicate layer (e.g. tetrahedral Si^{4+} by Al^{3+} or octahedral Al^{3+} by Mg^{2+}). The various sheets in clays bear charge on surfaces and edges, which are balanced by counter-ions in inter-layer spacing.

The number of exchangeable interlayer cations is also referred to as the cation exchange capacity (CEC). This is generally expressed as milliequivalents/100g, and ranges between 60 and 120 for relevant smectites. Variation in the amount, type and crystallographic origin of the excess layer charge results in a large family of natural (e.g. montmorillonite, hectorite, saponite) and synthetic (e.g. Laponite, fluorohectorite) layered silicates exhibiting different physical and chemical characteristics, such as layer size, stacking perfection, reactivity and Lewis acidity.

For example the lateral dimension of the layers range from 20 to 1000 nm. When exfoliated, an individual sheet is 1 nm thick, with aspect ratios (diameter to thickness) in excess of 100. Clays have very high surface area, of the order of hundreds of square meters per gram.

Montmorillonite is the most common type of clay used for nano-composite formation. However, other types of clay can also be used depending on the precise properties required from the product. For example, Hectorites (magnesiosilicates), which contain very small platelets. Similarly, synthetic clays (e.g. hydrotalcite) can be produced very purely and carry a positive charge on the platelets, in contrast to the negative charge found in montmorillonites. Figure 7 shows AFM images of montmorillonite nanoparticles.
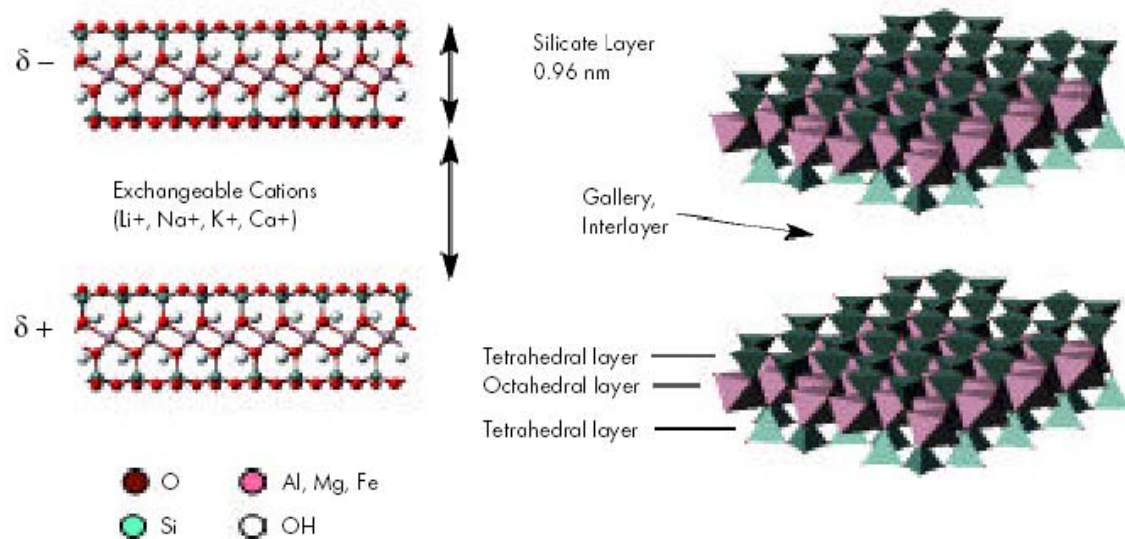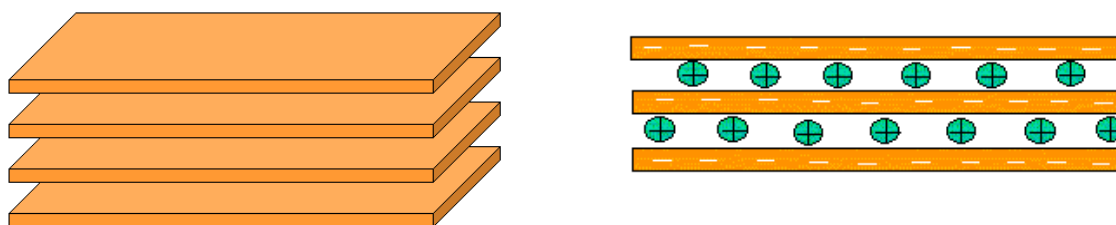
Figure 5: Composition of layers of clays.

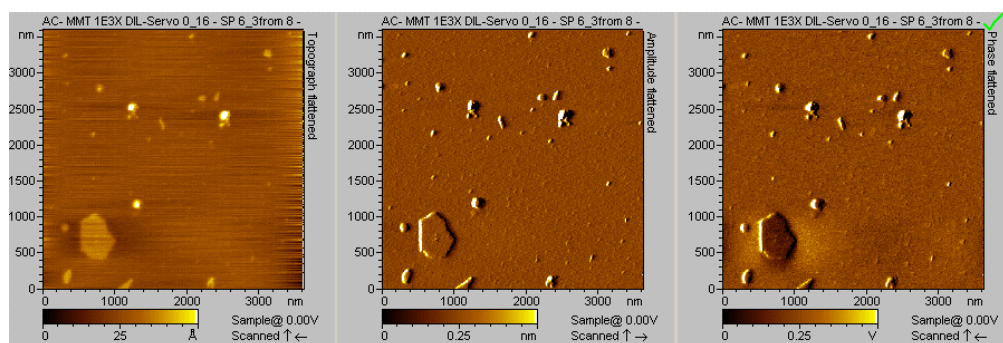*Figure 6: Sheet-like structure of clays.*

Figure 7: AFM images of montmorillonite show the high aspect ratio structure of clay particles.

Organic Pre-treatment and compatilibilization: All clays require some pre-treatment before they can be incorporated into polymers. This is because most clays are hydrophilic and incompatible with a wide range of polymers. It is necessary to make clays "organophilic" by ion exchange with an organic cation e.g. alkylammonium ion ("onium ion"). For example in montmorillonite, the sodium ions in the clay can be exchanged for an amino acid such as 12-aminododecanoic acid (ADA) in the following reaction:
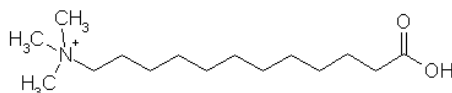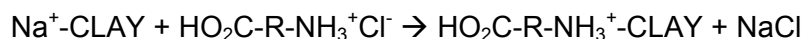
$$Na^+\text{-CLAY} + HO_2C\text{-R-NH}_3^+Cl^- \rightarrow HO_2C\text{-R-NH}_3^+\text{-CLAY} + NaCl$$

Figure 8: 12-aminododecanoic acid (ADA).

The exact way organic pre-treatment is done has a major effect on the formation of a particular nano-composite. Further development of pre-treatment chemistry is key to the future success of PCN's.

Types of clay composites: There are different modes of addition of clays to polymers. Intercalated or Exfoliated. In Intercalated the polymer penetrates the interlayer spacing of the clay without breaking the layered structure of the clay. In Exfoliated, the polymer penetrates thoroughly and breaks down the layered structure of the clay. This causes the clay layers to be evenly distributed within the polymer matrix. Whether an Intercalated or Exfoliated depends on a few factors that include the exchange capacity of the clay, the polarity of reaction medium, the chemical nature of inter-layer cations and the loading of inter-layer cations on the clay. Figure 9 below summarizes the various modes of clay addition to polymers.
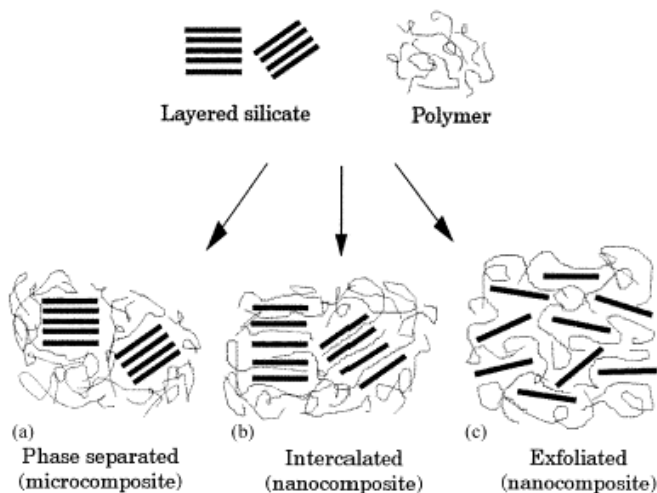

Figure 9: Different modes of addition of clay to polymers.

Factors determining composite type: Intercalated or exfoliated addition of clay depends on a variety of factors. Most important are: (i) The exchange capacity of the clay, (ii) the polarity of the reaction medium, (iii) The chemical nature of inter-layer cations and (iv) the loading of inter-layer cations on the clay. The chemical nature of the inter-layer cations (e.g. onium ions) is important because by modifying the surface polarity of clay, the onium ions allow the penetration of polymer pre-cursors into the inter-layer region. In addition, the ability of the onium ion to assist in the delamination depends on its polarity. The correct selection of modified clay is essential to ensure effective penetration of polymer/precursor and creation of intercalated or exfoliated nano-composites.

Polymer incorporation: The incorporation of the polymer can be done in two major ways:

First, the polymers can be incorporated directly through melt blending (extrusion) or solution blending. Melt blending depends on shear to delaminate and can be less effective in producing an exfoliated nano-composite than the second method, in-situ polymerization.

In the second method, a monomer is used for in-situ polymerization. This is the most successful method to date, though there are probably limits to its ultimate applicability. In-situ polymerization was first demonstrated by Toyota Central Research and Development Labs in 1980's[11]. The process has three steps (as shown in Figure 10 below): (i) Dispersal of ADA modified montmorillonite clay in nylon monomer (caprolactam), (ii) intercalation of monomer into the clay and (iii) in-situ polymerization to form exfoliated composite.
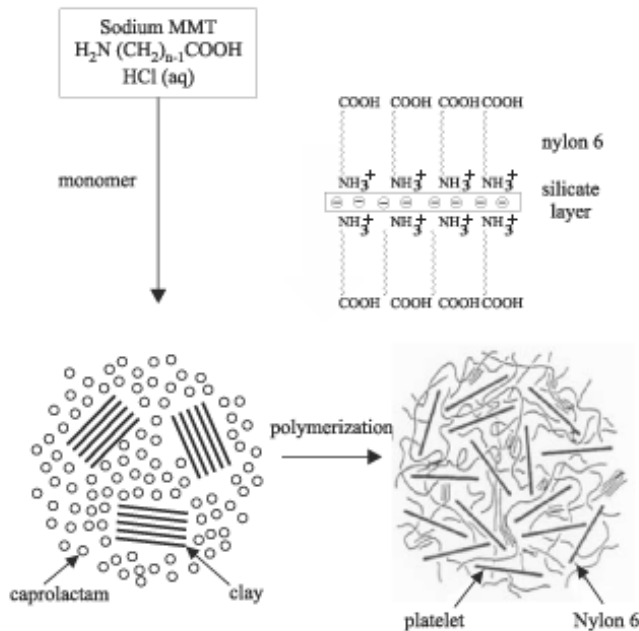

Figure 10: Formation of nylon 6 nano-composites by in-situ polymerization (Toyota process).

There have been many types of polymers used to create PCN's, including Nylons, Polyolefins, Polystyrene, Ethylene-vinyl acetate (EVA) copolymers, Epoxy resins,

Polyurethanes, Polyimides and Poly(ethylene terephthalate) (PET). An abridged list of polymers investigated with layered silicate includes polystyrene, various polyamides (6, 6-6, 11, 12, MDX), polyimides, polypropylene, ethylene vinyl acetate copolymers, poly(styrene-b-butadiene) copolymers (SBS), elastomers (PDMS, EPDM, NBR), polyurethanes, poly(ethylene oxide), poly(vinyl alcohol), polyaniline, epoxies, and phenolics. Alexandre et al. [5], Beal and Pinnavaia [2], and Krishnamoorti and Vaia [3] provide summaries of some of the polymers and fabrication routes available in the open literature.

Industrial activity in Polymer-Clay Nano-composites:

There is significant industrial activity in PCN's given the maturity of the field. Of the many companies active in the area, prominent ones include Nanocor and Southern Clay Products. Recently, General Motors and partners Basell, Southern Clay Products and Blackhawk Automotive Plastics announced external automotive body parts made from thermoplastic olefin layered silicate nanocomposites. A TPO nanocomposite with as little as 2.5% layered silicate is as stiff and much lighter than parts with 10 times the amount of conventional talc filler. The weight savings can reach 20 percent depending on the part and the material that is being replaced by the TPO nanocomposite. On a volume basis, the nanocomposite parts cost about as much as conventional TPOs because less material is needed to manufacture them and no new tooling is required to mold the parts. Overall, the weight advantage could have significant impact on environmental concerns and material recyclibility.

For example, it has been reported that widespread use of PLSNs by US vehicle manufacturers could save 1.5 billion liters of gasoline over the life of one year's production of vehicles and reduce related carbon dioxide emissions by more than 10 billion pounds [6].

Tech/Application	Estimated Market Size (2009)
Packaging	367 Million pounds
Automotive	345 Million pounds
Building/Construction	151 Million pounds
Coatings	63 Million pounds
Industrial	48 Million pounds
Other	67 Million pounds
Total	> 1 Billion pounds

Figure 11: Estimated market sizes (by 2009) for various applications of PCN's [29].

8.   Properties of Polymer-Clay Nano-composites

Addition of even relatively small amounts of clay improves the base properties of the polymers, and is therefore a quick and cost effective way to get specialty polymer performance from ordinary polymers. Efforts within the last 10 years have demonstrated a doubling of the tensile modulus and strength without sacrificing impact resistance for numerous thermoplastic (nylon and thermoplastic olefin {TPO}) and thermoset (urethane, siloxane and epoxy) resins through the addition of as little as 2 vol% layered silicate.

In general, nanoscale dispersion of the layered silicate platelets in resins produces glassy modulus enhancements of one to two times and rubbery modulus increases of 5-20 fold. Related increases in heat distortion temperature and enhanced elevated temperature mechanical properties (strength and modulus) are commonly reported. Additionally, reduced thermal expansivity (CTE), matrix swellability, gaseous permeability and flammability upon 1-5 vol% addition of exfoliated layered silicates will provide new opportunities for various resin systems.

These unique property combinations are observed with surprisingly low volume fraction additions of layered silicate (1-5%), thus maintaining polymeric processibility and reducing weight with respect to micron-scale counterparts (>20% loading).

Note that these comparisons are with regard to conventional filled polymers and not with regard to continuous fiber reinforced composites. Polymeric nano-composites may provide enhanced, multi-functional matrix resins, but should not be construed as a potential replacement for current state-of-the-art carbon-fiber reinforced composites.

In this section, the following properties of PCN's are discussed:

1. Modulus
2. Ductility
3. Coefficient of Thermal Expansion (CTE)
4. Flame retardance
5. Radiation shielding
6. Gas barrier

Nylon-Clay modulus vs. loading: Toyota initially experimented with such materials in 1980's where they used an in-situ polymerization process to add small quantities (5%) of montmorillonite to nylon-6. Even with small amounts of clay loading, significant property enhancements were seen. For example, 40% enhancement in tensile strength, 68% enhancement in tensile modulus, 60% enhancement in flexural strength, 126% enhancement in flexural modulus, and heat distortion temperature increase from 65 ^{o}C to 152 ^{o}C.

Figure 12 below shows more recent data [17] on the modulus of the Nylon-Clay nano-composite as a function of different loadings of clay for different types of Nylon polymer (LMW:Low Molecular Weight, MMW: Medium Molecular Weight and HMW: High Molecular Weight).
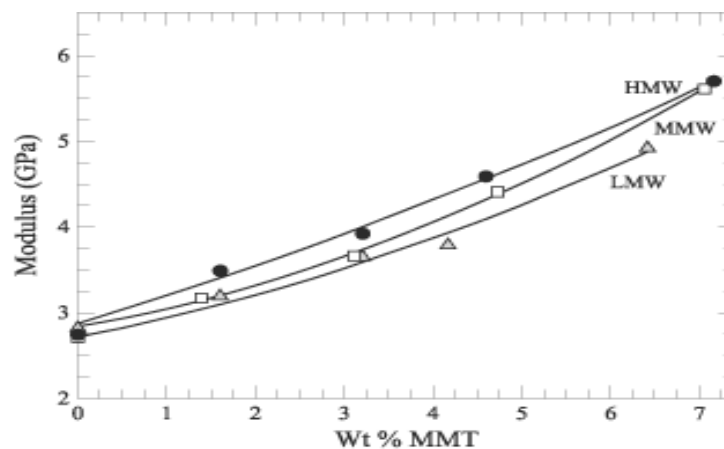

Figure 13: The modulus of Nylon-Clay composite as a function of weight percentage loading of clay for high (HMW), medium (MMW) and low (LMW) molecular weight nylon.

The modulus of the nano-composite increases monotonically as a function of the percent weight (loading) of montmorillonite. The figure shows that roughly 3% clay loading increases gross modulus (strength) by ~30% and 7% loading enhances the modulus by almost 100%.

Nylon-Clay ductility vs. loading: A similar study can be done of the effect of the addition of clay on the ductility of the nano-composite. Figure 14 shows the elongation at break as a function of the percent weight of montmorillonite in the composite material[17]. The plot shows the results for low, medium and high molecular weight Nylon. At 3% clay, ductility is still good, ~100% elongation at break.
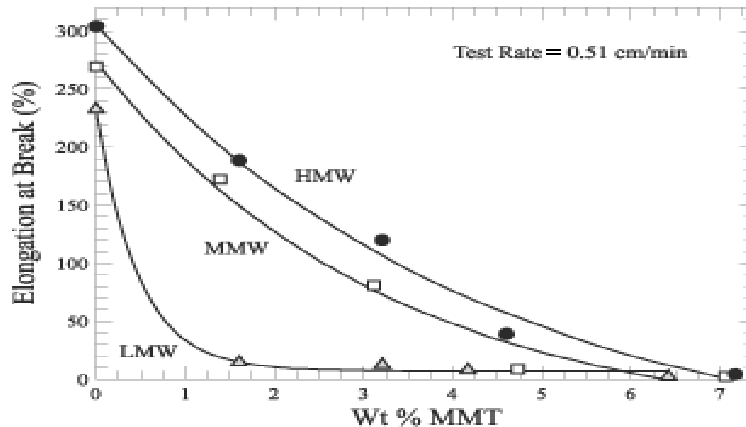

Figure 14: The elongation at breaking point of Nylon-Clay composite as a function of weight percentage loading of clay for high (HMW), medium (MMW) and low (LMW) molecular weight nylon.

Nylon-Clay CTE vs. loading: A similar study can be done of the effect of the addition of clay on the CTE of the nano-composite. Figure 15 shows the coefficient of thermal expansion (CTE) decreases as a function of the percent weight of montmorillonite in the composite material[17]. The plot shows the CTE for both rubbery (top) and glassy (bottom) regimes for low and high molecular weight Nylon. Adding clay reduces thermal expansion -- 3% clay, 20% decrease in expansion coefficient.
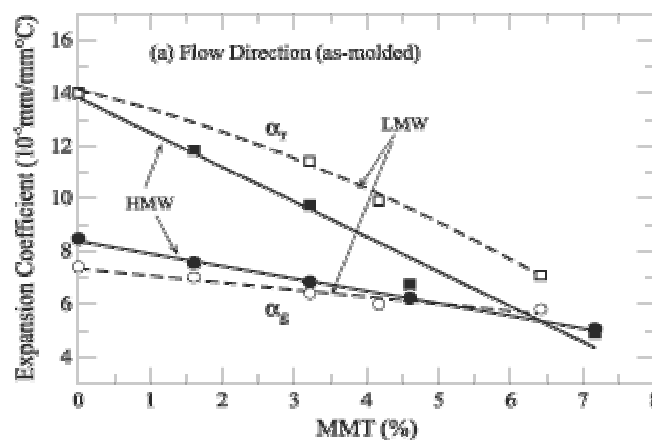

Figure 15: The thermal expansion coefficient of Nylon-Clay composite as a function of weight percentage loading of clay for high (HMW) and low (LMW) molecular weight nylon.

Polypropylene-Clay use as flame retardant material: A similar study can be done to investigate the flame retardant properties of PCN's. The figure shows the heat release rate for Polypropylene and its nano-composites with different fractions of clay loading[18]. For 5% loaded products, peak heat release rates are reduced by 70%.

A rapidly expanding area is fire retardant polyolefin nanocomposites. These materials readily form tough char layers. Char formation impedes the movement of volatilized polymer from the interior of a plastic matrix, denying fuel at the air/surface interface. For 5% loaded products peak heat release rates (HRR) are reduced by 70%. Employed in conjunction with traditional flame retardants, nanocomposites can achieve equivalent fire ratings using significantly reduced FR additive packages. With less FR additive dilution and greater reinforcement via nanocompositing itself, mechanicals are largely restored to levels seen in neat resin and at lower cost. This combination of benefits will likely make fire retardancy the largest use area long-term.
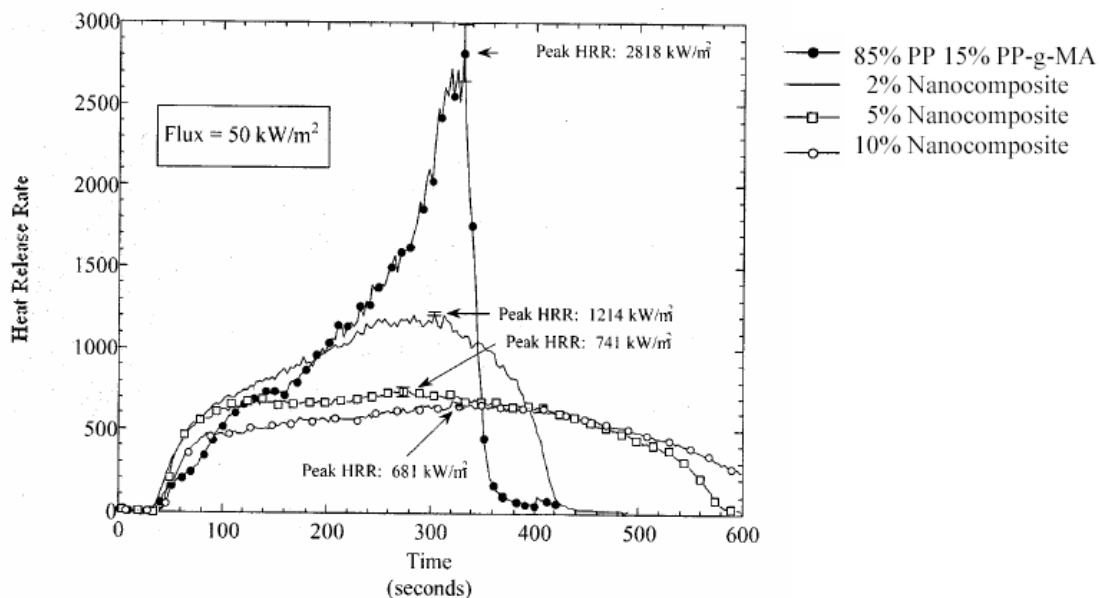

Figure 16: Heat Release Rates as a function of different amounts of clay loading in the nanocomposite.

Among others J.W. Gillman and collaborators have systematically studied the flammability of polymer/layered-inorganic composites, with the emphasis on polymer/ montmorillonite and polymer/ fluorohectorite hybrids [20—24]. Several polymer systems have been investigated using cone calorimetry studies, including nylon-6 [22, 24], bisphenolbased epoxies [22, 23], vinyl-esters [23], polypropylene [20, 23,24], and polystyrene [20,23, 24]. In these studies, cone calorimetry was used to measure the heat release rate and other flammability properties of the nanocomposites, under well-controlled combustion conditions. Both the polymer-layered silicate nanocomposites and the combustion residues were studied by transmission electron microscopy and X-ray di.raction [20]. Evidence was found for a common mechanism of flammability reduction, and it was also found that the type of layered silicate, nanodispersion, and processing degradation have an influence on the flammability reduction.

Potential use as radiation shielding material: Fig. 17 [29] plots the 5 cm depth dose equivalent (rem/yr) versus the absorber aerial weight (g/cm^2). In order of efficiency, liquid hydrogen, liquid methane, polyethelene and graphite are the best shield materials.

Low atomic weight materials, containing hydrogen and carbon, make good radiation shielding materials because of lower secondary radiation production. PCN's have high H/C content making them good potential radiation shielding materials.

GALACTIC COSMIC RAYS - SOLAR MINIMUM
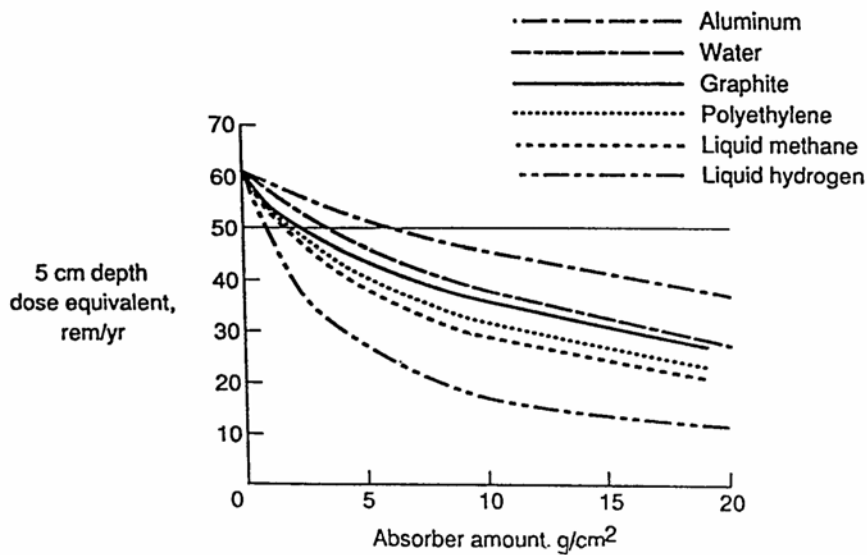### (Depth vs. Dose Functions for Selected Materials)

Figure 17: 5 cm depth dose equivalent (rem/yr) versus the absorber aerial weight (g/cm^2)

Gas-barrier properties of PCN's: Superior barrier properties of polymer/layered silicate nanocomposites against gas and vapor transmission have resulted in applications for food and beverage packaging, and for barrier liners in storage tanks and fuel lines for cryogenic fuels in aerospace systems.

Theoretically a very strong decrease of gas and liquid permeabilities is predicted [25], just by considering the permeant molecule's path around the filler particles [Figure 18(inset)]. The increase in path tortuosity as the small gas/liquid molecules have to diffuse around the impermeable solid fillers results in huge increases of the diffusion time, especially when fully exfoliated and oriented particles are considered [25].

Experimentally, a general decrease is also found in the gas and liquid permeabilities, as for example in the case of water vapor permeation through various polymer/mmt nano-composites. Even when the nature of the polymer and filler is varied from extremely hydrophilic to very hydrophobic, or even crosslinked systems (as PDMS networks reinforced by alkyl-ammonium), all of them show a dramatic decrease in water vapor transmission. Compared to the theoretical predictions the permeabilities fall between the behavior of a completely exfoliated nano-composite to a nano-composite which is intercalated.

The inexorable movement of plastics into packages formerly dominated by glass and aluminum creates demand for very low gas barrier plastics, which are easy to process in conjunction with common resins such as polyester. One such material is Nylon MXD6*. This semi-crystalline resin exhibits very good gas barrier. Its barrier is exceptionally good at high humidity. Converting MXD6 to a PCN further enhances barrier, making it superior to EVOH, the most commonly used high barrier resin. MXD6 nanocomposites were developed in conjunction with Eastman Chemical Company and are available directly from Nanocor under the tradename, Imperm^{TM}.

Imperm is appropriate for films, as well as multi-layer beverage and food containers. Oxygen barrier for films improves by 80% compared to neat MXD6. The barrier improvement in multi-layer PET containers is somewhat lower due to less-than-perfect platelet alignment during the bottle blowing process. Bottle oxygen barrier improves about 70% with bottle side-wall CO_2 improvement of 60% at ambient pressure. When the bottle is pressurized at 3 volumes CO_2 barrier improvement drops to slightly better than 40%.
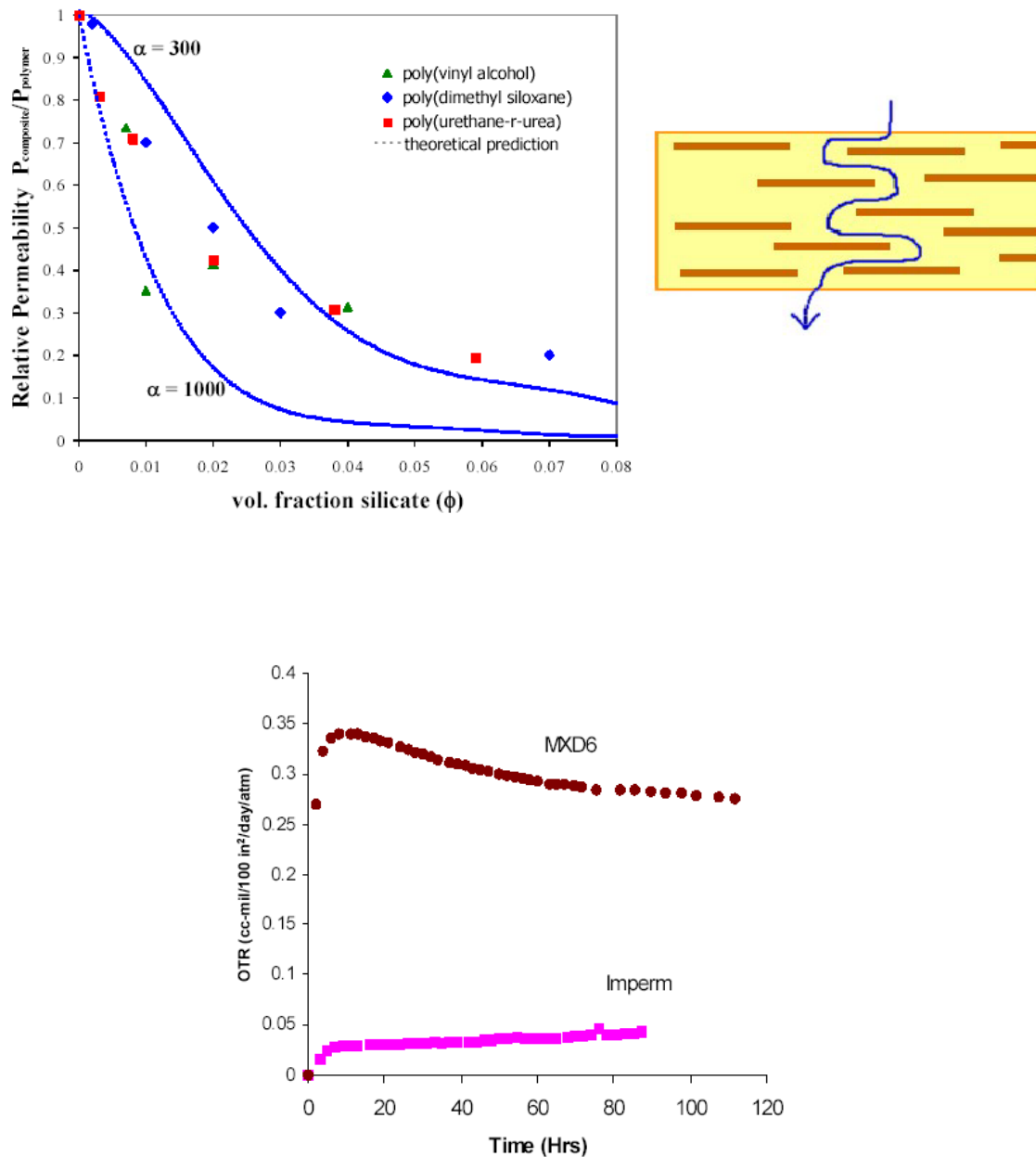
Figure 18: (Top) The relative permeability (permeability of composite divided by permeability of pure polymer) is plotted versus the volume fraction of the nm-thin inorganic filler. Water vapor permeability is measured for various systems and was compared with the theoretical predictions for filler aspect ratios of 1000 (completely exfoliated hybrid) and 300 (mixed exfoliated/intercalated structure). (Bottom) Gas permeability of Imperm compared to MXD6.

9.   Applications of PCN's in Aerospace/Defense

Clay/polymer nanocomposites have been considered as matrix materials for fiber-based composites destined for aerospace components. Aircraft and spacecraft components require lightweight materials with high strength and stiffness, among other qualities. Nanocomposites, with their superior thermal resistance, are also attractive for such applications as housings for electronics.

From the military perspective, these enhanced polymer systems provide opportunities in many venues. In addition to a general desire for higher-performance, higher use-temperature resins and thermoplastics, PCN's provide opportunities to address material limitations in advanced system concepts. Combinations of reduced impact resistance, CTE control, suppression of microcracking and increased modulus are currently being examined for next-generation nanoscale rigid-particulate reinforced resins for advanced fiber reinforced polymeric composites in unmanned aerial vehicles [12]. Thermal stability and enhanced fire retardancy through char formation have motivated investigation of PCNs as a component to anti-flammability additives for aircraft interiors [13]. Superior barrier properties against gas and vapor transmission have resulted in applications for food and beverage packaging for military rations [14] and for barrier liners in storage tanks and fuel lines for cryogenic fuels in aerospace systems. Also, depending on the type of polymeric host, PCNs display interesting ionic conductivity for solid-state electrolytes in batteries [15]. Finally, along with enhanced scratch resistance and ballistic performance, the nanoscopic phase dimensions and low volume fractions enable maintenance of optical clarity, critical for scratch-resistant face shields.

Recent efforts have begun to explore use of layered silicates as ceramic precursors that will react in-situ with aggressive environments to form a tough ceramic passivation layer on the polymer surface . Some examples of such self-passivation/self healing are during exposure to a solid-rocket motor exhaust (top) and plasma environments (bottom) [16]. Combinations of the self passivation response with CTE control provide unique alternatives to current materials being examined for inflatable membranes for space antennas and solar collectors. Survivability in real space environments is currently being examined for PCNs and other polymer nanocomposites through an exposure experiment on-board the International Space Station [17].

10. Summary: Why use PCN's for Aerospace/Defence

Aerospace is a Conservative industry:

- Complex systems level requirements:

    o Performance, Safety and Standards

- Long development times

    o Technology development to flight incorporation up to 10 years

- Risk averse – prefer to work in an evolutionary manner

    o Successive technology risk reduction

    o Alignment with industry standards and methods to accelerate adoption

Most Micro / Nanotechnologies (MNT's) are early in developmental stage:

- Technology risk:

    o Most MNT's are laboratory concepts, basic science issues remain

- Market risk:

    o Identification of path to commercialization is only beginning

    o Scalability and low-cost manufacturing issues not worked out yet

- Execution risk:

    o Scarcity of "done it before" teams, lack of appropriate industry experience and knowledge

PCN's are a mature technology:

- Proven Technology:

    o First applications in 1980's by Toyota

- Commercial validation:

    o Low cost

    o Applications in consumer (e.g. beverage bottles), industrial and transportation (automotive trim) industries coming to market.

- Industrial presence:

    o Established businesses focused on non-Aerospace/Defense applications

11. Prototype Identification and Potential Implementation Plan

Prototype Summary:

This paper proposes a PCN Program for rapid development of PCN's as a low cost multi-functional structural, fire retardant and radiation shielding materials. The development process will involve the discovery and validation of new PCN's that fit the specifications of Aerospace/Defense.

The program will proceed on multiple tracks simultaneously. First, it will involve partners from the Aerospace sector to actively identify their specifications for different applications. Second, the program will identify suitable PCN technologies that need to be investigated to fulfill the demands of Aerospace and non-Aerospace customers. Third, the program will launch a funded effort to develop the technologies that are suitable for identified end applications. Finally, the program will involve licensing agreements with research institutions as well as Aerospace and non-Aerospace partners to effectively transfer developed technologies for commercialization. The program will leverage CANEUS networks in aerospace/defense and nanotechnology research community to bring together customers, materials and simulation expertise.

Simulation-driven R&D strategy:

A unique part of the proposal is that the PCN discovery process will be driven by a simulation and modeling engine and various simulation methods developed by the program. The main R&D focus will be on the creation of a PCN simulation and modeling engine optimized for Aerospace/Defense applications.

The simulation engine will be used for:

1. Discovery of new PCN candidates and chemistries.

2. Simulation/Modeling of the properties of PCN candidates.

3. Investigation of manufacturing processes

4. Experimental creation and qualification of promising PCN candidates.

The simulation-based approach replaces the traditional experimental approach to solve the problem of identifying the right materials for an application. In the traditional approach, a la Edison, one has to systematically search through multiple materials candidates in order to identify the right candidates. This is a very slow, non-scalable and inefficient process, and as a result very expensive.

In comparison, the simulation approach is fast. It replaces replace years of experimentation with weeks or months of simulation, resulting in quicker design iteration. In addition, once a simulation engine is created, the process is relatively inexpensive and highly scalable. The creation of a successful simulation based approach requires

sophisticated computer modeling and high levels of materials knowledge. Once created however, it will result in a unique advantage for CANEUS.

The simulation engine will be based on existing theoretical and experimental data, and will be continuously updated with new data and simulation methodologies.

The basic process for an iterative simulation-driven approach for the program will be as follows, and is illustrated in Figure 19 below:

1. Use of simulation to find potentially interesting PCN candidates:

    Using the simulation and modeling engine, relevant PCN candidate classes will be identified. This identification will involve the prediction of the expected macroscopic properties of these candidates as much as possible. The prediction process will identify the candidates that conform to the various requirements for Aerospace/Defense applications supplied by the partners and collaborators of CANEUS.

2. Lab creation of best PCN candidates:

    Once the candidates have been identified, they will be created in co-operation with the various collaborative R&D partners. The process of lab creation of PCN candidates may itself be guided by the simulation engine in order to quickly identify the various reaction condition requires for high yield synthesis.

3. Lab characterization of best PCN candidates:

    The created PCN candidates will then be characterized and tested again in conjunction with the various collaborative R&D partners. This characterization will provide two key pieces of information. First, a test of the predictions of the simulation engine and second, a comparison of the properties of the PCN candidates with the requirements for various Aerospace/Defense applications. This data will help the optimization of the simulation engine as well as pointing out the changes needed to the PCN candidates.

4. Optimization of identified PCN candidates and model / discovery of new candidates:

    Finally, it will be determined what changes need to be made to the properties of the PCN candidates and what underlying changes in the polymers or the clays or both would be required to optimize the PCN candidates. For example, it may be determined that the addition of another function group in the polymer would improve the desirable properties of a PCN candidate. The simulation engine could be used to identify various changes required and this would bring the process back to Step 1 where optimized PCN candidates would then be identified.
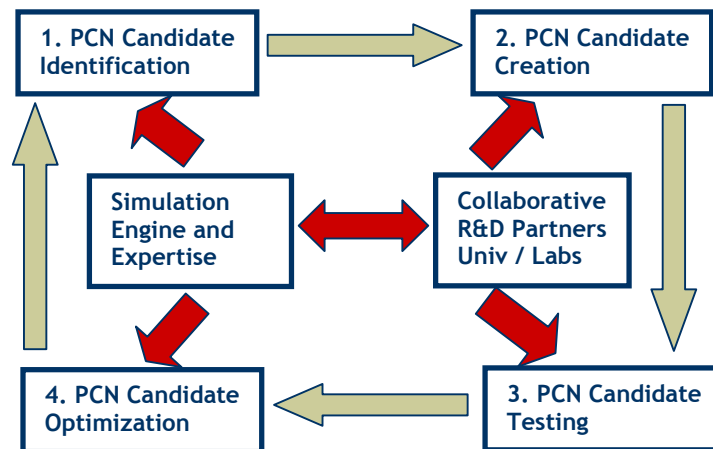
Figure 19: Simulation-driven R&D strategy to identify, create, test and optimize PCN candidates in conjunction with collaborator expertise.

Overview of R&D topics: A brief overview of the various aspects of the R&D effort is as follows:

1. Creation/optimization of modeling engine:

    This is of central importance to the whole R&D effort. This will involve the following steps:

    *   Development of first principle and approximation methods: These will be based on the existing methods and programs available for the simulation of existing PCN and polymeric materials and processes. These methods will be coupled with other ab initio and empirical methods to incorporate the various additives and processing steps required to create PCN's.

    *   Incorporation of experimental data: The simulation engine will have to incorporate as much existing experimental data as required in order to set the right baseline for the simulation engine.

    *   Incorporation of partner specs and optimization to material/property regimes of interest: Partner defined specifications on the desirable properties of PCN's will be incorporated in the simulation engine. Since PCN's will be primarily used within the regimes of partner-defined specifications, various methods may be employed in order to improve the predictability and speed of the simulation.

    *   Development of computational methods: Computational methods that are fast and scalable will be developed in order to run the simulations. This includes setting up the appropriate computer farms or systems required to run the simulations. It may be essential to parallel process the various steps of the simulation, and this would be addressed by this part of the development process.
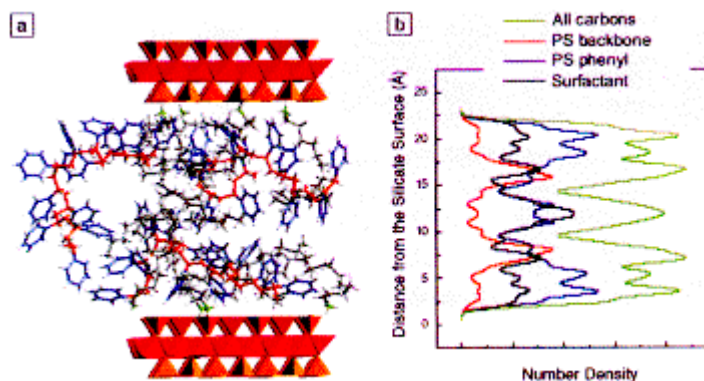
Figure 20: (a) Molecular Dynamics simulation "snapshot" of a silicate-surfactant-polystyrene nanocomposite. (b) The corresponding ensemble-averaged, number density of carbon atoms as a function of distance. (Courtesy Accelrys).

Monte Carlo and Molecular Dynamics simulation give insight into the structure of nanocomposites on the atomic level. Figure 20 reveals that when confined to a nanoscale gap or near a surface, the polymer chains order into discrete sub nanometer layers. This is useful in understanding the intercalation process and the source of some macroscopic properties such as ionic conductivity. Knowledge gained from simulations can be used to better engineer the polymer-silicate interaction.

2. Discovery of new PCN candidates:

There are multiple topics that will be explored; some of them have been listed below.

- A major challenge in developing nanocomposites for systems ranging from high-performance to commodity polymers is the lack of even simple structure-property models. Without such models, progress in nanocomposites has remained largely empirical. The large internal interfacial area between the polymer and the silicates together with the nanoscopic dimensions between nanoelements differentiates Polymer Nanocomposites from traditional composites and filled plastics.

- Investigation of usage of wholly synthetic organo-clays that are stable at temperatures greater than 400 ^{o}C. This will enable the creation of high temperature PCN's. The thermal stability of onium ions is a major limitation in the preparation of nano-composites from high temperature engineering thermoplastics. The use of more thermally stable imidazolium and phosphonium salts could improve the degradation temperature of organo-clays from 200-300 oC to more than 300 oC. Similarly wholly synthetic organo-clays can be made stable at temperatures greater than 400 C.

- Investigation of usage of new polymer systems e.g. high temperature resins. High temperature resins will also enable the creation of high temperature PCN's, and would enable low cost high performance polymers.

- Development of new compatibilization strategies for high temperature resins is critical to the development of high temperature polymers. The exact way organic pre-treatment is done has a major effect on the formation of a particular nano-composite. Further development of pre-treatment chemistry is key to the future success of PCN's.

- Exploration of potential addition of other nano-materials for additional performance enhancement. This may include the addition of nano-particles, carbon nanotubes and other kinds of fullerenes. The addition of other nano-materials may further enhance the desirable properties of PCN's. This would be one of the ways to optimize the properties of various PCN candidates.

- Exploration of covalent bonding of new materials to polymers or clays in PCN systems. The functionalization of polymers or clays may enhance the desirable properties of PCN candidates.

3. Modeling of PCN properties and processes:

As discussed in previous sections, some of the properties of interest are as follows:

- Structural

- Thermal

- Radiation shielding

- Barrier

- Manufacturing processes

4. Experimental creation and qualification of PCN candidates:

- Discovery and optimization of chemistry, aided by simulation engine.

- Characterization of properties and comparison with simulation.

- Understanding of discrepancies between simulation and experiment

R&D deliverables:

There are three major deliverables for the R&D effort undertaken in this program:

1. Simulation engine for predictive modeling of PCN systems

2. PCN candidates with properties suited to industry specs

3. Methods for large scale manufacturing

Intellectual Property:

The Intellectual Property developed under this work will be very important for CANEUS. There will be multiple avenues for ownership of intellectual property as well as for commercialization rights that will be used by CANEUS. First of all, CANEUS will own all IP that it develops directly or its academic partners develop under funded research. In some cases, IP will be jointly owned with research and industry partners. In addition, CANEUS will license key technologies from research institutions for multiple application areas, bundle the licensed IP with CANEUS owned IP and then license them to end customers in the Aerospace and non-Aerospace areas. CANEUS as an independent entity is in a unique position to license and own IP related to PCN's in multiple areas of application. In licensing IP to end customers, care will be taken to define areas of application so that same underlying technologies can be simultaneously applied in multiple areas.

Based on different areas of potential IP ownership, and connecting the dots with the deliverables of the R&D program, the IP ownership scenarios can be summarized as such:

1. Simulation engine IP can be owned wholly by CANEUS

2. PCN candidate IP owned jointly by CANEUS and collaborative R&D partner.

3. Manufacturing process IP owned jointly by CANEUS and appropriate industry partner.
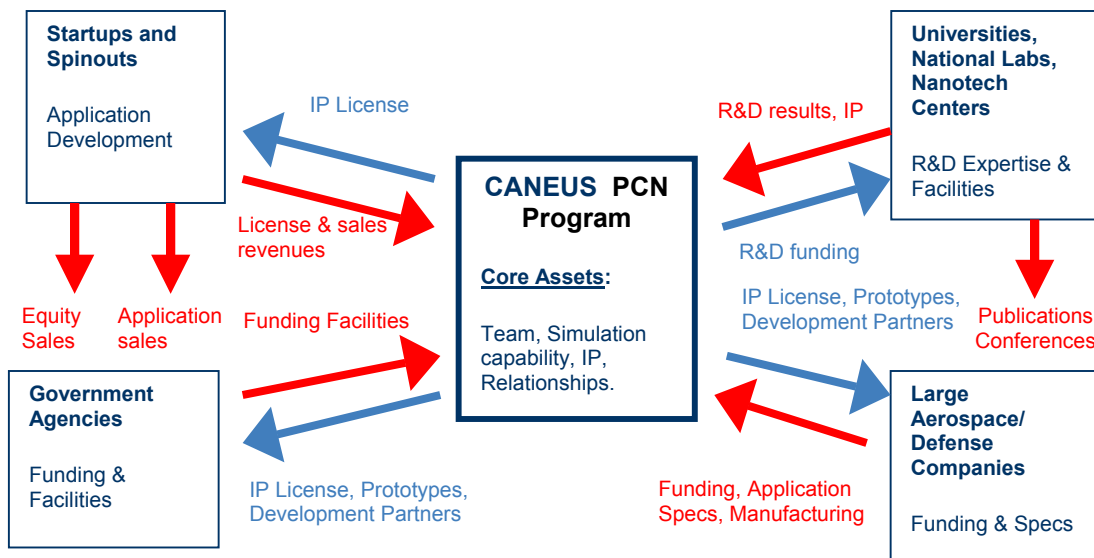
Partnership based program structure:

Figure 21: The various participants in the collaboration and their roles.

The prototype development program will proceed in partnership with Aerospace and academic collaborators. The Aerospace collaborators will identify the applications and their materials requirements. CANEUS will license base technologies from various research institutions, and work with the aerospace companies to identify their specs and to develop application prototypes. CANEUS will use the licensed technologies from research institutions to develop and optimize suitable pre-treatment chemistry, polymer and clay candidates and scalable manufacturing techniques. This development will occur simultaneously in programs overseen directly by CANEUS or at partner research institutions. Once developed, these commercially focused technologies can be licensed to Aerospace as well as non-Aerospace partners. CANEUS will get funding from government agencies and Aerospace companies for this development and commercialization work. This funding will also be used to license technologies and to fund directed research at various institutions.

Funding: We envision that the development of these technologies is a 3-year program, with commercial transfer process to begin at the end of 3 years and taking an additional year. Therefore the total project length will be 4 years. It will require a funding in the range of $2 MM per year for a total of $8 MM. The funding will be required primarily to build the simulation engine and to develop PCN prototypes. (Personnel, facilities, R&D support, and licensing.)

The program will require a strong participation from CANEUS organizations, as indicated, not only for participation in the research and commercialization but also in the funding. It is expected that private investors will provide about 50% of the required funding for the prototype development project and the remainder will come from government sources.

The corporate investors will primarily consist of Aerospace/Defense companies and Nano-composite materials companies. The government agencies will consist primarily of Aerospace/Defense agencies and State/local government agencies. Because of the strong emphasis on Aerospace and Defense sectors, it is envisioned that a large fraction of end product sales will be driven by government organizations.

Program Timeline:

The timeline for the program over the four years is given below for different years.

2005 (Specifications): The first year will focus on laying the groundwork for the program. Some salient milestones for the will be as follows:

- Get initial funding

- Sign-up industrial partners

- Define specs with industrial partners

- Create R&D collaborations

- Initiate work on simulation engine

2006 (R&D): The second year will focus on the completion of the simulation engine and on the creation of first PCN candidates. Some salient milestones for the will be as follows:

- Create simulation models

- Begin collaborative R&D

- License appropriate existing IP

- Continue to define specs with industrial partners

2007 (R&D): The third year will focus on the continual creation, characterization and optimization of the PCN candidates as well as the optimization of the simulation engine. Some salient milestones for the will be as follows:

- Refine simulation models

- Continue collaborative R&D

- Initial prototype tests with industry partners

- Industrial feedback for R&D

- Create licensing agreements

2008 (Commercialization): The fourth year will focus on building the foundation for a successful commercialization of the various technologies developed in the program as well as on the setting up of appropriate licensing and business relationships. Some salient milestones for the will be as follows:

- Licensing of technologies from R&D partners

- Evaulate spin-off opportunities

- Licensing and Technology transfer to Industry partners

12. Potential Investment Possibilities and Risk

The investors in this project would be comprised of government agencies and companies interested in advanced materials from the private sector. In the private sector, the companies could be end users in each industry segment or suppliers.

The investment criteria used by advanced materials companies vary depending on whether they are suppliers or users, whether the intended markets are military or commercial, and whether the end use emphasizes high performance or low cost.

Suppliers of advanced structural materials tend to be technology-driven. They are focused primarily on the superior technical performance of advanced materials and are looking for both military and commercial applications. They also tend to take a long-term view, basing their R&D investment decisions on qualitative assessments of the technical potential of advanced materials.

On the other hand, users tend to be market driven. They focus primarily on short-term market requirements, and they expect to recover their investments within 3 to 5 years.

Frequently, suppliers and users operate in both defense and commercial markets. However, the investment criteria employed in the two cases are very different. Defense contractors are able to take a longer-term perspective because they are able to charge much of their capital equipment expenses to the government, and because the defense market for the materials and structures is relatively well defined. Companies supplying commercial markets, on the other hand, must bear the full costs of their production investments and face uncertain returns. Their outlook is therefore necessarily shorter term. This difference in market perspective has hampered the transfer of defense-oriented materials technology to commercial users, and it underlines the importance of well-defined markets as a motivating force for industry investments in advanced materials.

The many applications of advanced structural materials do not all have the same cost and performance requirements. Accordingly, the investment criteria of user companies specializing in different product areas are different. In general, barriers to investment are highest in cost-sensitive areas such as construction and automobiles, where expensive new materials must compete with cheap, well-established, conventional materials. Barriers are lowest in applications that can tolerate high materials and fabrication costs, such as medical implants and aircraft.

The process of developing a new structural material and manufacturing products from it is very expensive, and may take 10 to 20 years. Most potential users require a payback period not longer than 5 years, and an initial sales volume of $5 million to $50 million per year to justify production investments. In general, commercial end users do not perceive that these criteria will be met by advanced structural materials, particularly in cost sensitive applications.

The high risk associated with this market uncertainty is the biggest single barrier to commercial production. The existence of well-defined markets for new structural materials appears to be a necessary but not sufficient condition to stimulate substantial investments by commercial end users.

We believe that in the choice of PCN's we have substantially reduced the technology risk and would significantly reduce the market risk through the involvement of industry partners as early as possible in the definition of the specifications as well as in the funding of the program.

Since PCN's have been used and applied in the Automotive and Consumer industries, the basic technology has been proven. This substantially reduces the technology risk, and provides a mature technology base to build new applications according to the specifications of Aerospace and non-Aerospace partners.

13. Next Steps for CANEUS

There are multiple steps for CANEUS to further support this program:

- Provide application and technical specification feedback

- Assist in team identification

    o Finding appropriate technical and business people

- Participate in fund-raising

    o Introductions to appropriate corporate and government investors

    o Assistance in applying for and receiving government R&D funds

- Help building broad-based industrial, governmental and academic collaborations

    o Strong leadership roles to be played by the CANEUS members

- Identify and provide key infrastructure

    o Some required R&D facilities/tools (directly from CANEUS or from partners)

    o G&A resources and office facilities

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