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Opportunities and Environmental Health Challenges Facing Integration of Polymer NanoComposites Technologies for Automotive Applications

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Abstract

The concept of nanostructured materials design is gaining widespread importance among the automotive industry. Although employment of nanotechnology in current and future automotives will go long way in solving energy crises, it is necessary to understand both the hazards associated with nanomaterials and the levels of exposure that are likely to occur. The existing knowledge in these areas is quite limited and it will be necessary in the near future. This paper highlights these key issues and goes a long way in pointing recent activities on environmental risks of nanomaterials. Some research directions are given and existing automotive opportunities and applications explored.

Key words: nanocomposites, automotive, polymer, environmental health

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1. Introduction

Nanoparticles, when engineered appropriately, exhibit a variety of unique and tuneable physiochemical properties. These characteristics have made engineered nanoparticles central components in an array of emerging technologies with widespread potential applications in material sciences and engineering. Large quantities of nanomaterials are already commercially available for commercial scale applications due to the establishment of well-developed nanomaterial production methods such as chemical vapour deposition method and electrospinning. As a result more practical applications are being uncovered due to the ease of bulk manufacture.

Carbon nanotubes, carbon nanofibres, and polyhedral oligomeric silsesquioxanes (POSS) are being used commercially in nanocomposites [1, 2]. Nanoclays, however, are the most dominant commercial nanomaterials, accounting for nearly 70% of the total volume of nanomaterials commercially used [3-5]. The first clay nanocomposite, polyamide-6/montmorillonite clay nanocomposite is known to be developed by Toyota back in 1993 [6, 7]. Since then, the concept of nanostructured materials design has gained widespread importance in automotive industry mainly due to low cost and availability, as compared to other nanomaterials such as POSS and carbon nanotubes. Automotive and packaging market segments are presently expected to account for nearly 80% of total nanocomposite consumption. Conservative estimates predict an annual growth rate of 10-15% with an expected products market volume of €500 billion (Figure 1) and components including nanoporous materials, formulations, nanocomposites, thin films and coatings, market volume of approximately €50 billion for 2010 [3-5].

Figure 1

In particular, the nanotechnology machinery segment is expected to grow by 30% per annum [5]. According to estimates by the Lux Research group, the market potential of nanotechnology products could be worth up to around €1.9 trillion by 2014 [3-5].

The use of nanomaterials in current and future automotives will allow environmentally friendly automotive materials with higher performance and low manufacture costs, as discussed in the following subchapters. However, nanotechnology might also have detrimental effects to environment and it is paramount to understand both the hazards associated with nanomaterials and the levels of exposure that are likely to occur, while still taking advantage of the technology. The important unknowns include, but not limited to, the environmental effects of nanomaterials from manufacture stage to applications and to recycling; accidental releases/exposure; risk assessment paradigm and the level of uncertainties at each of the mentioned stages; and, the actual environmental benefits of specific nanomaterials is unclear. In addition, appropriate environmental standards are required. Currently only limited information is available on hazards of nanomaterials and it will be necessary to generate and establish new resourceful data in the future. This paper then highlights some of the key issues associated to the use of the nanomaterials in automotive industry. It further points the reader to recent comprehensive works in the subject matter. Research directions are also suggested and conclusions are drawn.

2. Current opportunities and applications in automotives

2.1 Interior and exterior applications

Although problems with dispersion and exfoliation of nanoclays in polyolefins have been an obstacle to growth, significant progress has been made over the past years. Today, automotive applications continue to be a driving force in nanoclay growth. The use of

polypropylene (PP)/clay nanocomposite by General Motors to fabricate the step-assist for two of its 2002 mid-size vans (GM's 2002 model GMC Safari and Chevrolet Astro vans) represented a significant milestone in the commercialization of polymer nanocomposite technology [2]. This was the first commercial automotive exterior application for a polymer nanocomposite based on a 'commodity' plastic, such as polypropylene (PP), polyethylene (PE) or polystyrene (PS)/poly(acrylonitrile, butadiene styrene) (ABS). As such, the introduction provided a major boost to confidence in the commercial reality of nanocomposites.

At present, polyolefin nanocomposites are a large, fast-growing market with many innovations in diverse applications [8]. Commercial applications include automotive interiors, appliance and electronic housings and power tools [1]. These applications, however, rely on the lightweight, high performance and cost effectiveness of the advanced thermoplastic polyolefin (TPO) material. For example, it was claimed that replacing the step-assist (previously made from conventional talc-reinforced material [2]) with the nanocomposite material, in which the filler comprises nanometre-thick flakes of highly exfoliated ultrapure clay, results in weight savings on structural parts by >10%, with increased stiffness, improved ductility at cold temperatures and enhanced appearance. Generally, parts made with TPO material with as little as 2.5% inorganic nanofiller are as stiff as those with ten times the amount of conventional talc filler, while being much lighter; weight savings can reach upto 20% depending on the part and the material that is being replaced by the TPO nanocomposites [3-5, 9].

In addition, the improved properties of the nanocomposite matrix material may upgrade the properties of relatively low cost composites up to the level of high performance composites and further increase the temperature resistance of existing high-performance composites. The added cost of the nano-filled matrix can be lower due to the low amounts of filler

necessary for a significant improvement. For instance, a low MW nanocomposite can replace a high MW unfilled polyamide 6 (PA 6). The other advantage of using polymer nanocomposites as compared to that of different polymers to improve the high temperature behaviour of fibre composites is that the properties can be improved without any change in the melting temperature and processing conditions [10, 11].

2.2 Under-the-hood applications

In polyamide under-the-hood (bonnet) applications, nanoclays raise modulus and heat deflection temperature without loss in elongation [12]. Studies by researchers at Toyota demonstrated a 168% increase in room temperature tensile modulus, a 87°C increase in heat distortion temperature (HDT), and a 40% decrease in water permeability of polyamide-6/clay nanocomposites over unmodified polyamide-6 [6, 7]. These property improvements were attributed to a significant volume of polymer chains constrained by their interaction with the exfoliated clay lamellae. Nevertheless, the nature of the constrained region as the mechanism of reinforcement has yet to be satisfactorily explained and property improvements have yet to be confirmed on commercially available nanocomposites using standard processing techniques. In automotive applications such as side mouldings, trim and panels in General Motor's vehicles, nanoclay compounds have advantages including reduced weight, a wider processing window, improved colourability and improved scratch and mar resistance. A consequential research focal point that has emerged relates to the known deleterious effects of the automobile exhaust air pollutant NO_x on nylon-6 [13], in efforts to protect the nanocomposite from degradation.

2.3 Fuel systems

Multi-wall carbon nanotubes (MWCNT) have been used commercially as a conductive additive for plastics since the early 1990s. Dispersion of MWCNTs can be accomplished on commercial equipment and does not require surface treatments. One application in fuel system components is to increasingly move towards conductive resins. MWCNTs have been used in polyamide-12 for fuel system components and are being investigated in other resins such as polyphenylene sulfide (PPS) [14]. In fuel lines, MWCNTs improve/introduce conductivity while preserving elongation and barrier properties. Retention of barrier properties and durometer is an advantage in seals and gaskets for the automotive, chemical processing and electronics industries. Other markets for CNTs include semiconductor applications in automotive electronics, in which CNTs have the benefit of cleanliness and low-sloughing and, in automotive exterior body panels to enable electrostatic painting.

2.4 Bioplastics

The end of life vehicle (ELV) directive in Europe states that by 2015, vehicles must be constructed with 95% recyclable materials. 85% of which must be recoverable through reuse or mechanical recycling and 10% through energy recovery or thermal recycling [15]. Despite significant improvement in properties, disposal and recycling problems, combined with environmental and societal concerns make continued use of petroleum-based nanocomposites unattractive. It is expected that increased use of green nanocomposites made using renewable and environmentally benign materials such as biofibres and biobased resins derived from soybeans, pure cellulose acetate, citrate based plasticizer, and organically modified montmorillonite nanofillers for example will prevail [16]. Notably, many of the major car manufacturers such as Daimler Chrysler, Mercedes, Volkswagen,

Audi Group, BMW, Ford and Opel now use biocomposites in various applications as demonstrated in Figure 2 [9].

Figure 2

Interior trim components such as dashboards and door panels using polypropylene and natural fibres have been produced for Daimler Chrysler for sometimes now. The use of flax fibres in car disk brakes to replace asbestos fibres is also another example. In 2000 Audi launched the A2 midrange car in which door trim panels were made of polyurethane reinforced with mixed flax/sisal mat. Daimler Chrysler has been increasing its research and development in flax reinforced polyester composites for exterior applications for a number of years now [17]. Mercedes also used jute-based door panels in its E-class vehicles in 1996 [18]. Cotton fibres embedded in polyester matrix were used in the body of the East German “Trabant” car [19]. Some other applications include under floor protection trim of Mercedes A class made from banana fibre reinforced composites, and the Mercedes S class automotive components made from different bio fibre reinforced composites [20]. Upgrading these greener composites through biodegradable bioplastic-nanocomposites remains the most feasible route to environmentally friendly green nanocomposites using extrusion followed by compression moulding or injection moulding. By employing nanomaterial much of this objective can be achieved. In particular, incorporating a small amount of appropriate compatibilizer is expected to enhance miscibility of composites matrix and clay nanofillers and thus further improve mechanical and thermal properties of the nanocomposites. These nanocomposites may ultimately replace existing petroleum-based polypropylene/thermoplastic polyolefins (PP/TPO) in automotive applications.

Further, Daimler–Benz has been exploring the idea of replacing glass fibres with natural fibres in automotive components since 1991 [9]. Mercedes Benz pioneered this concept with the "Beleem project" based in Sao Paolo, Brazil, through which, coconut fibres were used in the commercial vehicles over a 9-year period. Evidently nanoclays are being used to replace other fillers and provide an improved balance of stiffness and toughness while reducing weight. For example, 5% of a nanoclay can replace 15-50% of standard fillers like calcium carbonate thereby reducing the cost and improving the mechanical properties. Nanoclays typically replace talc or glass fillers at a 3:1 ratio, with 5-8% of a nanoclay replacing 15% of glass filler, for example [21]. The balance of flexural modulus and impact strength in nanocomposites allows polyolefins to compete with engineering materials like PC/ABS. Notably, polyolefin nanocomposites are less expensive and do not need drying, resulting in a 15-25% system cost savings over some engineering resins.

2.5 Advanced automotive de-pollution catalysts

Another opportunity of nanostructured materials lies in advanced automotive de-pollution catalysts. Currently, more than 95% of vehicles produced in the world are equipped with a catalytic converter, which, for the gasoline-fuelled engines, is almost exclusively based on the so-called three-way catalyst (TWC) [22]. TWCs are capable of simultaneously and efficiently converting CO, hydrocarbon (HC) and NO_x into harmless CO_2, H_2O and N_2, provided that the so-called air-to-fuel ratio (A/F) is constantly kept at the stoichiometry, i.e., under conditions where the amount of oxidants is equal to that of reducing agents. Since the advent of the TWCs, in the early 1980s, there has been a progressive tightening of the environmental legislation aimed at minimizing the amount of harmful pollutants emitted during the vehicle use [23]. For example, by the end of the 1960s, uncontrolled emissions of 40–60 g of CO/km were common to most of the passenger vehicles; this

amount decreased to 2.3 g CO/km in 2000 and was phased down to 1 g of CO/km in 2005 by European legislation (Euro phases 3 and 4). These limits represent reduction of 94–96% and 97–98% respectively as compared to uncontrolled emissions. Later on, US Tier 2 legislation, issued by EPA, challenged even more the catalyst/vehicle producers: besides the quite restrictive limits on the emissions, durability as high as 120,000 miles (about 180,000 km) was phased-in by 2004 [24].

The current EPA targets certainly represent a tough task making necessary the development of new materials with enhanced thermal stability as far as ignition emissions are concerned. This is due to the fact that TWCs feature the so-called light-off type of conversion vs. temperature behaviour, where the conversion steadily increases from 0% to 100%. The light-off temperature, conventionally taken as corresponding to 50% of conversion, is typically 267–328º C. To achieve the improvement of efficiency as required by the EU and US legislation, the catalyst heating time, i.e., time to reach light-off temperature, must be decreased down to 10–20 s. A cost-effective solution is to mount a secondary converter directly on the exhaust manifold [25]. This, however, exposes the catalysts to extremely harsh conditions, where temperatures as high as 745º C are reached. In this respect, the most feasible solution is by adopting an appropriate design of the CeO_2–ZrO_2 system, nanostructured materials of high thermal stability that are suitable for next generation automotive converters. For example, by nanostructuring CeO_2-containining hexaaluminates via a reverse microemulsion synthesis, thermal stabilities up to 856º C could be achieved [26].

2.6 Automotive engine applications

Reduction in the weight of engines is a key factor in improving the fuel efficiency. The use of lightweight materials has become more prevalent as car manufacturers strive to reduce

vehicle weight in order to improve performance, fuel and oil efficiency, and to reduce emissions [27]. By obviating the need for liners automotive engines, the engine dimension can be significantly reduced. It is estimated that direct weight savings of about 1 kg per engine can be easily achieved [28, 29]. Also, elimination of liners allows reduction in the overall dimension of engine [28-30]. Every kilogram reduction of payload is important for improvement in fuel efficiency. Reduction of about 110 kg in a typical automobile of weight 1100 kg will improve fuel economy by 7% [31]. In the lifetime of a car this reduction of engine weight is significant. [32]

Presently, most manufacturers have replaced cast iron (density=7.8 g/cm^3) engine blocks with lightweight and low-cost aluminium-silicon (density=2.79 g/cm^3) crankcases. Several Al-based alloys and metal-matrix composites, such as A319Al, A356Al, A390Al and A360Al, are in use. However, inadequate wear resistance and low seizure loads have prevented their direct usage in the cylinder bores. The cylinder bores of these aluminium alloy blocks are usually made of cast iron liners because of their good operating characteristics such as wear resistance. These liners need to have a specific wall thickness, which results in a relatively large web width between the individual cylinder-bores, and increases the dimensions and weight of the engine. Moreover, mechanical friction is of another concern that needs to be addressed. Piston system is a major contributor to engine friction [33]. The cylinder bore/piston and piston ring friction constitute nearly all of the piston system's friction losses [33]. A major portion of oil consumption arises from bore distortion and poor piston ring sealing resulting from ring and bore wear. Aluminium exhibits a transition from mild to severe wear when the nominal contact stress exceeds a threshold value [34]. Presence of reinforcement particles does prevent such transition until higher threshold values. Such a situation can arise due to two following factors: (1) start of ignition where oil has not spread over entire surface and (2) bore distortion. Thus, to

continue using aluminium alloy engine blocks (due to lighter weight) and to improve wear resistance of the engine bore surface several techniques to form new composite and/or monolithic coating on the bore surface, have been explored. Figure 3 illustrates other potential areas for coatings for improving engine efficiency [35].

Figure 3

There are currently many other examples where nanocomposites coatings are engaged. For instance, one of the most important properties of automotive clear coats is their scratch resistance [36]. The scratch resistance of a coating is even more important in refinish coating because the cars are normally used very soon after paint application so that the coating does not have enough time to reach its ultimate hardness. Although several methods have been utilized to improve the scratch resistance of coatings, the application of nano-fillers is one of the most widely used methods for improving the mechanical properties of polymeric coatings [27, 33, 34]. Clean, environmentally friendly and cost effective sol–gel processes are being introduced for enhancing the corrosion resistance of different magnesium alloys too [37]. Novel modified silane nanocomposite protective barrier coatings obtained mixing two sols separately prepared (a pre-hydrolysed 3-glycidyloxypropyl trimethoxysilane (GPTS) with acidic catalyst and another obtained from tetraethylorthosilicate/methyltriethoxysilane (TEOS/MTES)) using sol–gel route as protective barrier coatings for aluminium alloys with potential automotive applications [38, 39]. Low-friction and low-wear behaviour of diamond-like amorphous nanocomposite coatings, also in humid environments, enables industrial applications of these coatings as hard, self-lubricating coatings on sliding parts in the automotive industry [40].

3. Environmental, health and risk assessment issues with nanocomposite material

Paracelsus (1493-1541) stated "all things are poison and nothing is without poison", therefore it is the amount or dose of a substance that determines whether it is poisonous or toxic [41]. The question then is how the amount of nanomaterials dose should be determined. Bulk materials are regulated by weight in the European Union [42], however the same amount of a nanoscale form of the material will not have the same properties as the bulk material. It has been suggested that using the surface area to volume ratio of a nanomaterial for regulation may be more accurate.

To date, specific engineered nanomaterials have been studied for health and environmental impacts including titanium dioxide [43, 44], carbon nanotubes [45, 46], and silica [47]. However, the nature of the biological interactions between nanoparticles and cells/tissues is not known [48]. For instance, early stage research indicates that both single- and multi-wall carbon nanotube exposures may have injurious cellular effects, Figures 4 and 5 [49-51].

Figure 4

Figure 5

They can enter the human body in various ways, reach vital organs via the blood stream, and possibly damage tissue, however nanodiamonds (another nanoscale carbon form) show little toxic effect when added to neuronal and lung cells [52]. There are a myriad of nanoparticles, varying both in morphology and chemistry, that may be industrially relevant and toxicological studies have only been considered on a small proportion of these, there are many other types of nanoparticles of which there is little or no information, such as polyhedral oligomeric silsesquioxanes (POSS) and nanoclays (which are more widely used

in automotives already). The potential toxicological effect becomes more complicated when nanoparticles are combined with different engineering materials for multiphased interfaces.

Nanoparticles properties are likely to differ from those of the bulk material due to volume scaling, surface area scaling and specific size effects. These changes in physicochemical properties, combined with their smaller size, will mean that the nanoparticulate form of a material will interact differently to the bulk material with biological environments. It is therefore insufficient to consider the nanoscale form of a material using the same data on the material safety data sheet (MSDS) as the bulk material. This also has severe consequences on determining the safety of the nanoparticle form of the material (which is dependent on the exposure and environment of the material). The safety of nanoscale materials for humans and the environment is an area of international concern and great debate (e.g. Refs. [53, 54]. There is currently a lack of knowledge of the effect on the toxicity of the physicochemical attributes, the biological macromolecular interactions (e.g. with DNA), the possibility of nanomaterials playing a carrier role, the likelihood of translocation, the agglomeration of particles, the chemical composition of the material, and the adequacy of the existing toxicity tests. The combination of these characteristics of nanomaterials presents a hurdle for the risk assessment of engineered nanomaterials, which is acknowledged by many regulatory and industrial bodies, e.g. Nanotechnology Industries Association (http://www.nanotechia.co.uk/). The toxicology and risk assessment of engineered nanomaterials is discussed further elsewhere [54-57].

4. Environmental impact of engineered nanoparticles

The environmental consequences associated with the ultimate disposal of these materials also need to be evaluated carefully [58]. Crane and Handy [57] considered in depth the environmental exposure, toxicity testing and risk assessment of manufactured nanomaterials and concluded that there is little empirical information on the ecotoxicity or bioaccumulation potential of nanoparticles, and that a number of studies currently available, do not consider the likely exposure (e.g. dose and solution) which will have an effect on the ecotoxicity of the material.

As nanotechnologies move into large-scale production in automotive and other industries, it is an increasing possibility that the accidental release of engineered nanoparticles into the environment will occur. There are many possible scenarios where accidental exposure can occur throughout the production, use and disposal of the nanoparticles and the products that they are used in. Release can occur during manufacture, storage, and transportation of the nanomaterials, their end products and waste products (e.g. waste water during production and erosion at end of life) with release into air, soil and water. There are an increasing number of studies on this complex subject (e.g. [59, 60]).

5. Structural testing facilities

As discussed earlier, there currently exists a high demand for high performance lightweight structures for automotive and motorsports applications. Carbon/glass/natural fibre-reinforced composites meet these requirements and can be easily tailored to enhance their strength and performance [8, 11, 61]. Therefore, there is an increase in the amount of composites structural testing in the structural testing laboratories across the globe as scientists and engineers search for lighter, stronger and cheaper materials to build the

desired structures. Unfortunately, fibre-reinforced nanocomposites hold some environmental and health concerns. This fact is well documented in open literature and carbon/glass fibres are widely classified as potential biohazards. As a result, personnel working with composites normally wear body, ear, face, and, head protection apparatus when work is in progress. In structural testing laboratories as the one shown on Figure 6 where tests such as energy dissipation or crush testing occur, the current practice is to allow the carbon dust settle after the test followed by vacuum cleaning to clear the debris.

Figure 6

It is highly likely that some of these dust particles are of nanoscale sizes and can potentially settle in the open air for a long time. In addition to the already identified potential biohazards and environmental pollutions, the key question arising is on if the existing personnel protection against composite dust particles is protective enough. A research direction is emerging demanding further research on the dust particle sizes, shapes, solubility, and distribution concentrating on engineered particles at nanoscale.

6. Concluding remarks

Stringent environmental policies, economic competitiveness, depleting fossil fuel resources and environmental concerns have driven the automotive industry to explore newer avenues to improve efficiency of automotive engines. Various techniques have been adapted to achieve this goal. Such include use of specially designed nanomaterials to allow the engine to operate at higher temperature with reduced external cooling (heat removal) thus fuel efficiency can be improved significantly. The incorporation of several different types

of fibres into a single matrix has led to the development of hybrid biocomposites. Other methods to improve fuel efficiency are to use lightweight material to reduce load, reduce heat losses due to exhaust and conduction through engine body and to reduce frictional losses. The automotive applications remain a driving force in nanoclay growth, making automotive industry a leader in these particular nanomaterials.

One of the principal attributes of nanoparticles enabling development is their unique catalytic properties, tailorability of their physical properties and ease to alter solubility or dispersion. However, the same physicochemical properties that give them industrial utility may also confer activity in biological systems. This is probably the biggest drawback facing the nanocomposites technology in automotives industry. In this sense, the toxicology of these nanoparticles has to be evaluated under environmental, health and occupational exposure including biocompatibility. Health, safety and environmental risks that may be associated with products and applications of Nanotechnology and Nanosciences (N&N) need to be addressed upfront and throughout their life cycle [62]. Doing complete lifecycle analysis on newly developed products, and considering all the ecological as well as the socio-economic components, will help to ensure growth of nanomaterials in automotive industry. It should be noted that fundamental to the success of nanotechnology is its perceived safety by the public. There are a number of urgent needs related to use of nanomaterials some of which have ben discussed in this paper. Enhancing our understanding of nanomaterials-human-environmental interface is important so as to develop a contingency plan. In particular, more research studies are required to feel a knowledge gap in aspects that affect human health and pollute environment directly.

For future research directions, there is a potential for unexpected interactions between nanoscale materials and biological systems due to their size, chemical properties and/or

availability with a major issue being the risk assessment of industrial nanoparticles on human health and the environment. As research activity shifts from basic manufacturing applications to wide range auto parts, fluids, coatings etc, there exists an urgent need for environmental and health studies on nanoparticles to elucidate the possible risks.

Currently there is a drive to determine whether specific nanomaterials pass the skin/brain/blood barriers in the body and whether it is possible that they can translocate within a biological environment. Research is necessary to understand what is unique about the health risks of engineered nanomaterials and what *'representative'* nanomaterials can be used for toxicity analysis. Research to address life cycle assessment of nanomaterials used in high performance structures and other related activities are also required.

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Caption of Figures

Figure 1 Global trends in nanomaterials applications. Source: Sustainable Chemistry Strategic Research Agenda 2005

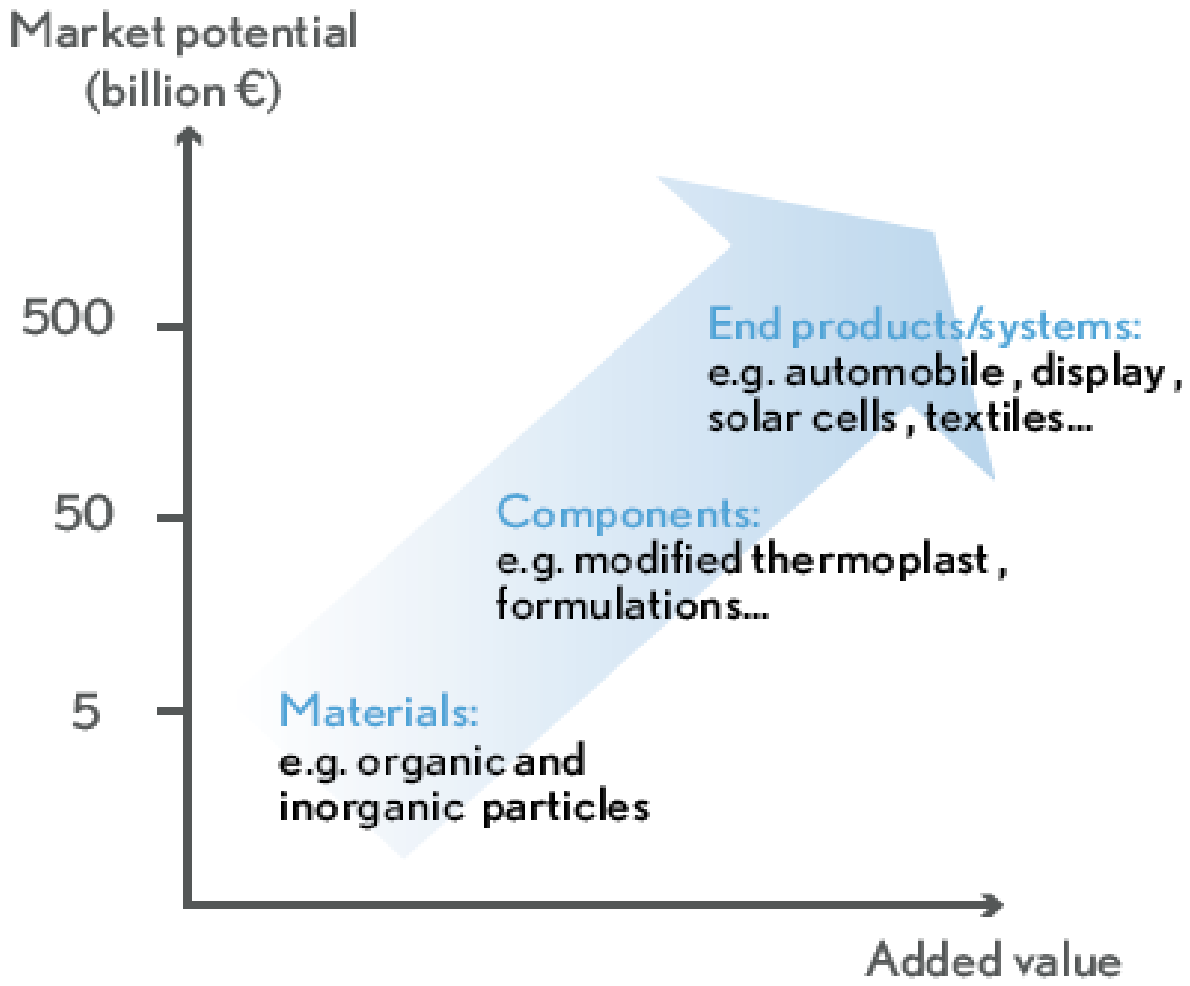
Figure 2 Typical applications of biplastics in modern car [9].

Figure 3 Role of coating in improving efficiency of engine [35].

Figure 5 Effect of on the dispersion of carbon nanotubes (CNT) grinded in rat cells. Intact CNT remained mainly entrapped in the large airways and ground CNT were better dispersed in the lung tissue (arrows) [49].

Figure 6 Effect of filament decoration on cell toxicity in H596 cells. The growth curves obtained from chemically decorated MWCNTs and CNFs are denoted De-MWCNTs and De-CNFs, respectively. The filament concentration to which all samples were exposed to was 0.02 *í*g/mL. In both cases, the number of viable cells is lower in the decorated samples, indicative of increased toxicity [48].

Figure 7 Carbon/glass fibre particles in an impact testing lab, small samples testing (right) in a typical structural crush test laboratory



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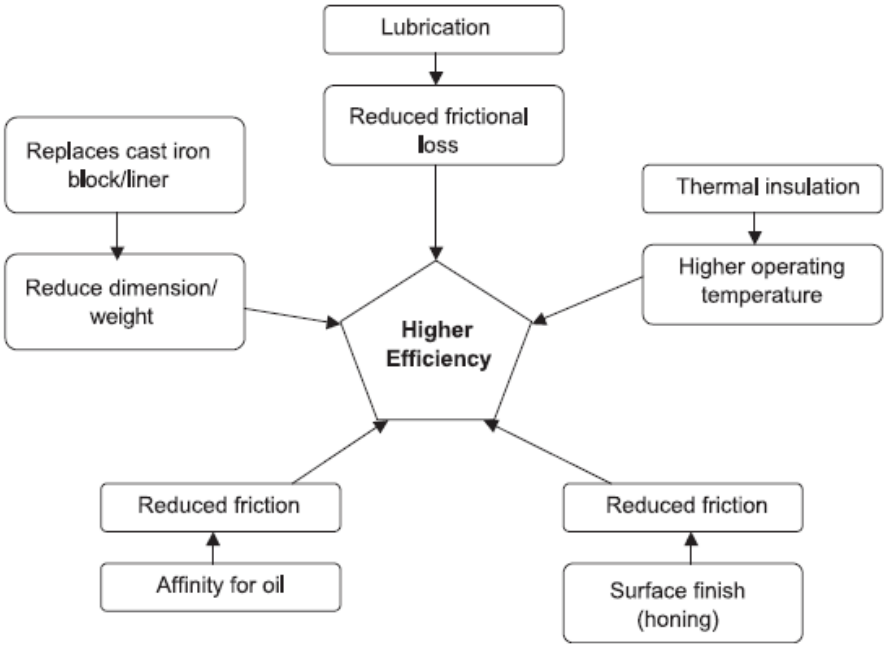

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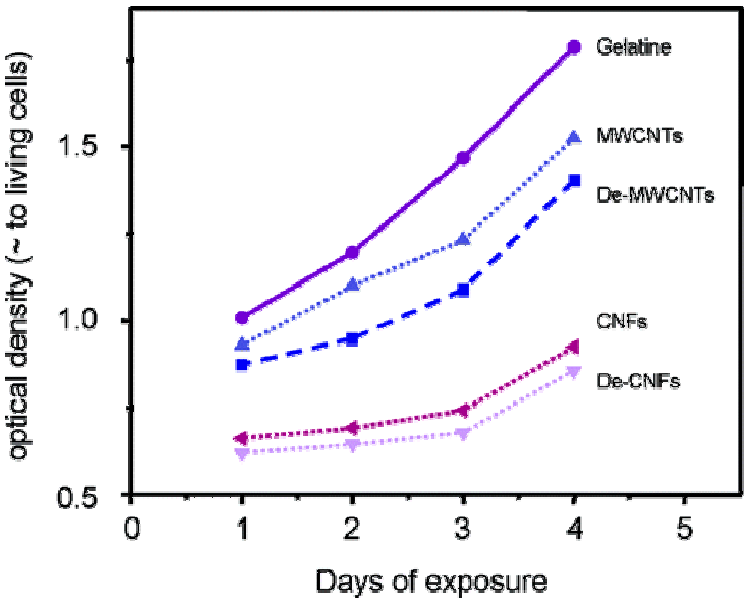

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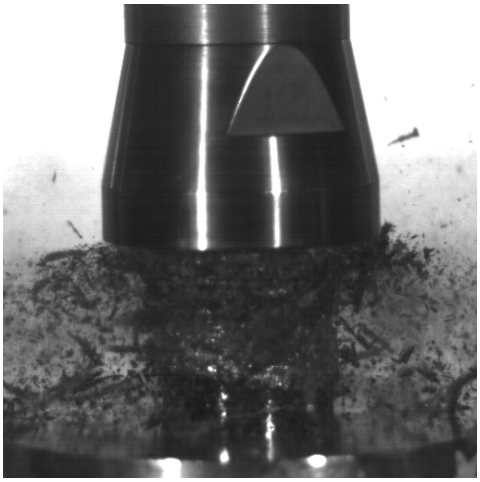

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