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Nanocomposites for automotive: enhanced graphene-based polymer materials and multi-scale approach

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Abstract: The present initiative provides a summary overview on Graphene Related materials (GRM) for automotive applications and investigates efficient ways to integrate Graphene as polymer reinforcements within composite materials for energy-efficient and safe vehicles (EESVs). An approach that starts from the nano-scale through the Graphene elaboration by experiments to meso/macro-scale by continuum mechanics modelling is discussed with respect to some limiting factors in terms of the large scale production, the interfacial behaviour, the amount of wrinkling and network structure. Finally, a strategy for modelling such a composite is elaborated in the framework of the Graphene Flagship to well understand such limitations for a full applicability of Graphene. It is anticipated that this initiative will advance innovative lightweight graphene composites and their related modelling, designing, manufacturing, and joining capabilities suitable for automotive industry which requires unique levels of affordability, mechanical performance, green environmental impact and energy efficiency. This leads to complete understanding of the new graphene composites and their applicability in high-volume production scenarios.

Keywords: Automotive applications, Composite modelling and design, Energy efficient and safe vehicles, Graphene, Graphene composites

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and multifunctional materials. Dr. Azoti is a research member of the applied sciences faculty of University of Sunderland, UK.

1 Introduction

The automotive industry is a large and critical sector within the global economy. However, the global automotive industry is currently facing great challenges, such as responsibility for increasing annual CO_2 emissions, lack of strong decarbonisation targets, and safety issues. The development and manufacture of environmentally-friendly, EESV is a great solution to these challenges (Figure 1). The most effective way to enhance fuel consumption and to decrease CO_2 emissions is producing lighter vehicles. However, vehicle safety is usually compromised due to light-weighting. Due to the trade-off between light vehicles and safety standards, new directions need to be adopted to overcome safety issues. Several attempts have been made to strengthen vehicle structure to enhance crashworthiness, however, safety issues remain the main obstacle to producing lighter and greener cars. Therefore, the need to discover a new direction for greener and safer vehicles is urgent.

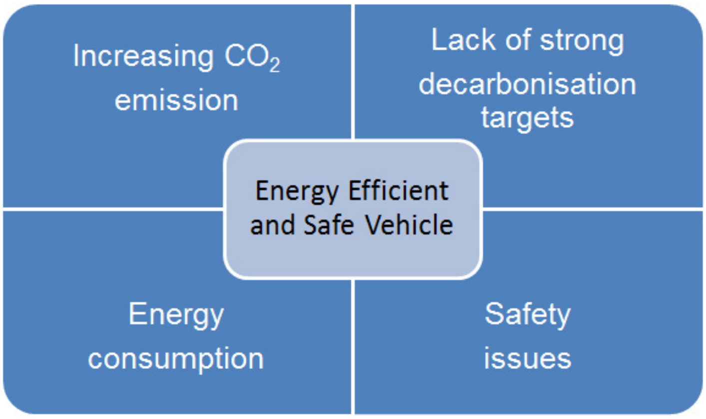

Figure 1: EESV and its compromising targets.

Recently, Graphene has attracted both academic and industrial interest because it can produce a dramatic improvement in properties at low filler content. Graphene is expected to have plenty of potential applications and the most immediate application for Graphene-based products is to be used in composite materials. The particular example of polymer nano-composites or polymer matrix composites which incorporate nanoscale filler materials could be highlighted. Indeed, Graphene-based polymers show substantial property enhancements at much lower loadings than polymer composites with conventional micron-scale fillers (such as glass or carbon fibres), which ultimately results in lower component weight and can simplify processing. Moreover, the multifunctional property enhancements made possible with nano-composites may create new applications of polymers. It has been found that by dispersing a small amount (%) of graphene in polymers, many properties of the resulting composites, such as tensile strength and elastic modulus, electrical and thermal conductivity, thermal stability, gas barrier, and flame retardance can be significantly improved. Based on these multifunctional properties, graphene/polymer composites are promising as both structural and functional composites that can be widely used in various important fields. The previous mentioned properties make graphene-based polymers and composites good candidate for structural materials, with integration of functionalities, within automotive sector. This initiative aims to analyse novel Graphene-based composite materials and their potential applications in automotive industry. To this end, the utilisation of Graphene in the fabrication of nano-composites with polymer matrices is investigated. Modelling, and design strategies are explored to enhance both vehicle and occupant safety; yet remain very light.

2 Graphene composites at present in the automotive segment

The automotive industry is widely viewed as being the industry in which the greatest volume of advanced composite materials will be used in the future to produce light vehicles. Nowadays, several advanced materials are widely used in automotive industry. Because of its multifunctional properties and promising applications, many expectations in composite materials are related to Graphene.

However, no application of graphene-based materials is currently marketed in the automotive sector. Therefore, research activities are under development for study the potentiality of these systems and all the value's chain of automotive needs to be involved in this effort. One of the most challenge aim is the economic impact of the innovative structures on the vehicle market, all the value's chain have to address their effort to get as low as possible the final cost of the innovative products.

From some recent experiments and numerical simulations, it has been clarified that the impact resistance and crashworthiness optimisation studies of advanced composites components remain at an early stage. The Graphene-based polymer composites are still in infancy stage with regard to high-performance structural applications. There are no theoretical studies available in the technical literature on dynamic analysis and crash behaviour, as well as the fracture and failure behaviour of Graphene composites under severe loading conditions typical for automotive applications. Also, the reliability of determining the homogenised response of such materials depends upon the ability to accurately capture the interfacial behaviour between the Graphene and the polymer matrix. A large amount of work remains to be done to develop a practical, reliable and capable tool to analyse and design the new Graphene-based polymer composites and study the crashworthiness optimisation for its structures and their applications in the automotive industry. Therefore, automotive sector looks forward innovation activities on this topic to assess its potential use for different applications both for structural and functional potentialities.

3 Material challenges

Graphene is expected to have plenty of potential applications and the most immediate application for graphene is to be used in composite materials. Though numerous challenges remain in developing a fundamental understanding of Graphene Related Materials (GRM) materials and their polymer composites, these materials have already been explored for a range of applications. Many properties of Graphene reinforced polymer composites for instance the tensile strength and elastic modulus, electrical and thermal conductivity, thermal stability, gas barrier, and flame retardancy are significantly improved.

However, to take full advantage of its properties for applications, integration of individual Graphene in polymer matrices is prime important. Many factors, for instance the type of Graphene used and its intrinsic properties, the dispersion state of Graphene in the polymer matrix and its interfacial interactions, the amount of wrinkling in the Graphene, and its network structure in the matrix can affect the final properties and applications of Graphene-based polymer composites (An et al. (2010)). Thus, the following challenges are facing the automotive engineers and researchers:

- Lack of new methods of large scale production of graphene based products - mechanical exfoliation is not scalable to an industrial process;
- Lack of new methods of functionalization;
- Investigation of the exfoliation process of graphene based material during the process;
- Expected low ductility of graphene-based composites structure. Considering implementation on several vehicle components (i.e. front end), this will lead to high vehicles' deceleration, which minimising the vehicle safety;
- Insufficient knowledge on attainable strength/stiffness of graphene thermosets/ thermoplastic polymer composites;
- No existed materials model on commercial explicit finite element software to model graphene based composite materials for high performance structural applications;
- Graphene-based composite material characterisation and modelling still not fully investigated especially with regard to automotive applications and different loading conditions;
- Lack of knowledge on graphene composites for high performance structural applications and interface properties between the graphene and polymer matrix under severe loading condition (i.e. fragmentation and crash);

- Preparation of automotive composites-Lack of knowledge on how to design in graphene composites automotive structures that can offer high stiffness, strength and predictable and safe failure modes;
- Nowadays vehicle and body architectures do not usually take advantage of the essential qualities of new composite materials;
- Some approaches to joining and bonding of graphene-based composites parts insufficiently covered by simulation and modelling tools; no automotive experience available;
- The joining of dissimilar materials is not covered by an appropriate know-how and several critical points are not yet solved by the scientific community and researcher;
- Great attentions focused on embedded CO_2 in overall LCA within lightweighting process; however, no solid info on how to evaluate pro's and con's inside design process.

3.1 Large scale dispersion techniques

A key consideration when targeting the large scale production of Graphene nano-composites is the extent to which we can extrapolate the laboratory scale results in order to predict the properties of Graphene-reinforced polymers produced on a large-scale. Often the laboratory scale composites are produced using "ideal" Graphene i.e. known to contain only one or two layers. In reality, as we look to scale the Graphene production process, the likelihood is that we will produce material with a distribution of layer thicknesses. The question then is: what effect does the number of layers have upon the properties of the composite? This has been studied recently by Gong et al. (2012), who used Raman spectroscopy to firstly characterise the Graphene (in terms of number of layers) and also to monitor its subsequent deformation during atomic force microscopy (AFM) nano-indentation experiments on polymer composites, by utilising stress-induced shifts in the Raman bands.

This method has previously shown that individual flakes of Graphene have the capability to reinforce a polymer matrix but, interestingly, the recent work by has Gong et al. (2012) has shown that bi-layer Graphene would be equally as good as monolayer Graphene, whilst tri-layer Graphene would only show a 15% reduction in reinforcing efficiency. Furthermore, it is only when the number of layers is >7 that the reinforcing efficiency of Graphene falls to less than half that of monolayer Graphene. If we consider the Graphene interlayer spacing in relation to the dimension of the polymer coils (which would separate the layers in a polymer composite), however, it can be shown that higher volume fractions of Graphene can be obtained for the multi-layer material than for monolayer Graphene. Therefore there is a balance to be struck between the ability to achieve higher loadings and the reduction in reinforcing efficiency as the number of Graphene layers is increased.

In addition, the best method of producing Graphene to be introduced in composites for industrial applications is the reduction of graphite oxide in controlled conditions. The chemical or thermal reduction of Graphene oxide can produce Graphene with a large number of defects, reducing the quality of the final product and worsening the expected properties. Without introducing functional groups, reduction of graphite oxide produces Graphene with different percentages of oxygen, a good quality Graphene need to have less than 2.5% of oxygen and preferable less than 1% of oxygen. However, the presence of oxygen helps to introduce new functional groups through chemical reaction such as covalent reactions (nucleophilic substitution, electrophilic substitution, and condensation and addition reactions) and non-covalent reactions (Kuila et al. (2012)). The direct chemical reaction in pristine Graphene involves the use of powerful chemical reactions like radical reactions or the use of dienophiles to react with the C-C bond (Georgakilas et al. (2012)).

3.2 Modelling of Graphene-based composite materials

The number of theoretical/numerical works published on Graphene-based composites has so far been limited. A variety of techniques could be used in modelling the Graphene-based composite materials; however, the clear integrations between these techniques are still not clear for some applications (i.e. high performance structural applications). Much of the previous works has focused on modelling the elastic modulus at a set temperature. Since temperatures vary widely in space, a temperature-dependent model is required for the elastic modulus. In general, there are two main approaches taken when modelling Graphene composites. The first focuses on the molecular level interactions. Molecular models use simulations to determine local interactions among atoms or chemical reactions between the matrix and nanotubes (Frankland et al. (2003)). Molecular models are limited to very small systems due to their high computational cost. The second is continuum modelling which considers overall deformations. Continuum models include the Mori-Tanaka model, rule of mixtures, and the Halpin-Tsai model (Hashin and Rosen (1964)). Multi-scale models, which combine molecular and continuum models, have also been developed. Models by Wang et al. (2006) should be cited.

Examples of existing works in this field are, for example, the molecular dynamics-based simulation techniques employed by Awasthi et al. (2009), who studied the load transfer mechanisms between polyethylene and a Graphene sheet. Cho et al. (2007) employed a Mori-Tanaka approach to study the elastic constants of nano-composites with randomly distributed Graphene sheets. Most recently, Montazeri and Rafii-Tabar (2011) developed a multi-scale finite element model to study the elastic constants of a Graphene-based polymer nano-composite. Parashar and Mertiny (2012) also proposed a multi-scale model using finite elements to characterise the buckling phenomenon in Graphene-based polymer composites.

4 Graphene flagship initiative for a better understanding of the use of graphene in the automotive industry

The Graphene flagship initiative through the **i**nnovative **G**raphene-based Polymer **C**omposite materials for **Auto**motive applications propose to combine novel materials concepts with the latest safety design approaches through the development and optimization of advanced ultra-light graphene-based polymer materials, efficient fabrication and manufacturing processes, and life-cycle analysis to reduce the environmental impact of future vehicles.

The development of novel graphene-based materials and their potential applications in automotive industry are one of the main focuses of the EU Graphene Flagship project. This initiative allows the utilisation of graphene-based materials in the fabrication of nanocomposites with different polymer matrices to be investigated, modelled, and designed, as candidate for structural applications, to enhance both vehicle and occupant safety; yet remain very light (Figure 2). This material will provide benefits such as improved strength, dimensional stability and better thermal behaviour, better flame behaviour (active as flame retardant and for reducing the emission of smoke), and superior durability. It has been clarified that the impact resistance and crashworthiness optimisation studies of advanced composites components remain at an early stage.

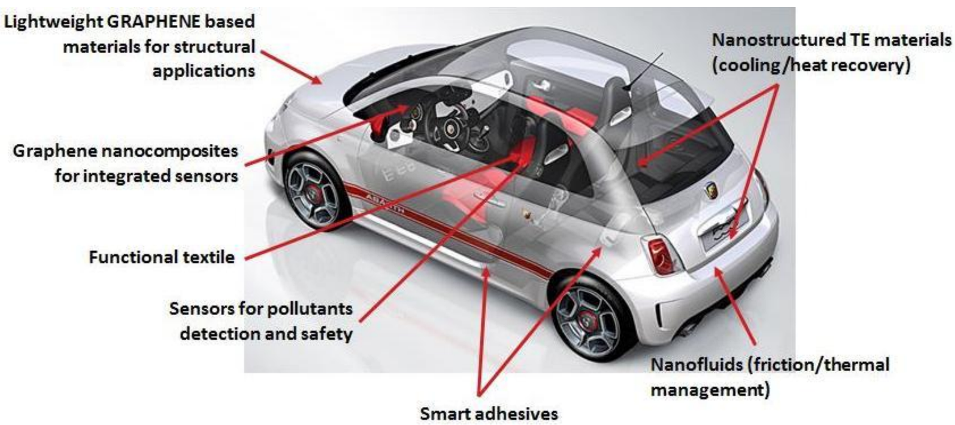

Figure 2: Potential applications of Graphene-based composite in automotive

The initiative also focuses on the development of advanced graphene-based materials for vehicles, contributing to an accelerated market introduction of new energy-efficient and safe vehicles (Figure 3). It is a project targeted at achieving radical advances in graphene-based composites that show high performance parts for transport applications. With a consortium combining industrial partners through the value chain - from basic material and composite manufacturers to automotive suppliers and end-users - and the leading European universities and research centres working on composite materials, it assures these breakthroughs are achievable and will have strong uptake in industry. The context will allow monitoring all the innovations in this field collaborating with a broad and competent partnership ranging from academic basic research to the suppliers of materials for the production of the final automotive components.

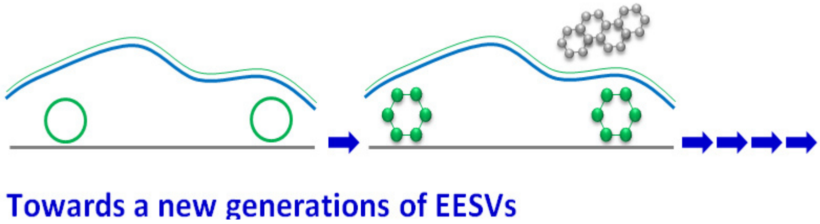

Figure 3: Moving towards Graphene-based composite Car.

4.1 Approach

This initiative is complex and multidisciplinary by nature. In order to successfully reach the technical objectives of the work, a holistic approach is adapted to include a wide range of activities spanning from material development and new synthesis to final products and new joining and fabrication technologies as shown in Figure 4.

4.2 Developments

Below are recent developments with regard to the current work within the Graphene Flagship:

- Full understanding of and control over the novel graphene-based composites, allowing us to integrate all desired characteristics into one composite material, develop and investigate new graphene-based products and graphene-based polymer composites characterisation; properties and low cost production of graphene-based polymer materials with unique syntheses;
- Understanding of and control over approaches for homogeneously incorporating graphene-based products nanofillers that can be cost-effectively dispersed into the abovementioned composite material systems. These nanofillers will improve material properties such as mechanical performance (e.g. toughness) or dimensional stability (e.g. less shrinkage) ideally by integration of these elements into a pre-produced fibre material preform or in the resin;
- Development of a large scale-production method for graphene-based on a microwave heating or synthesis of precursors followed by subsequent quenching to exfoliate graphene-based products flakes;

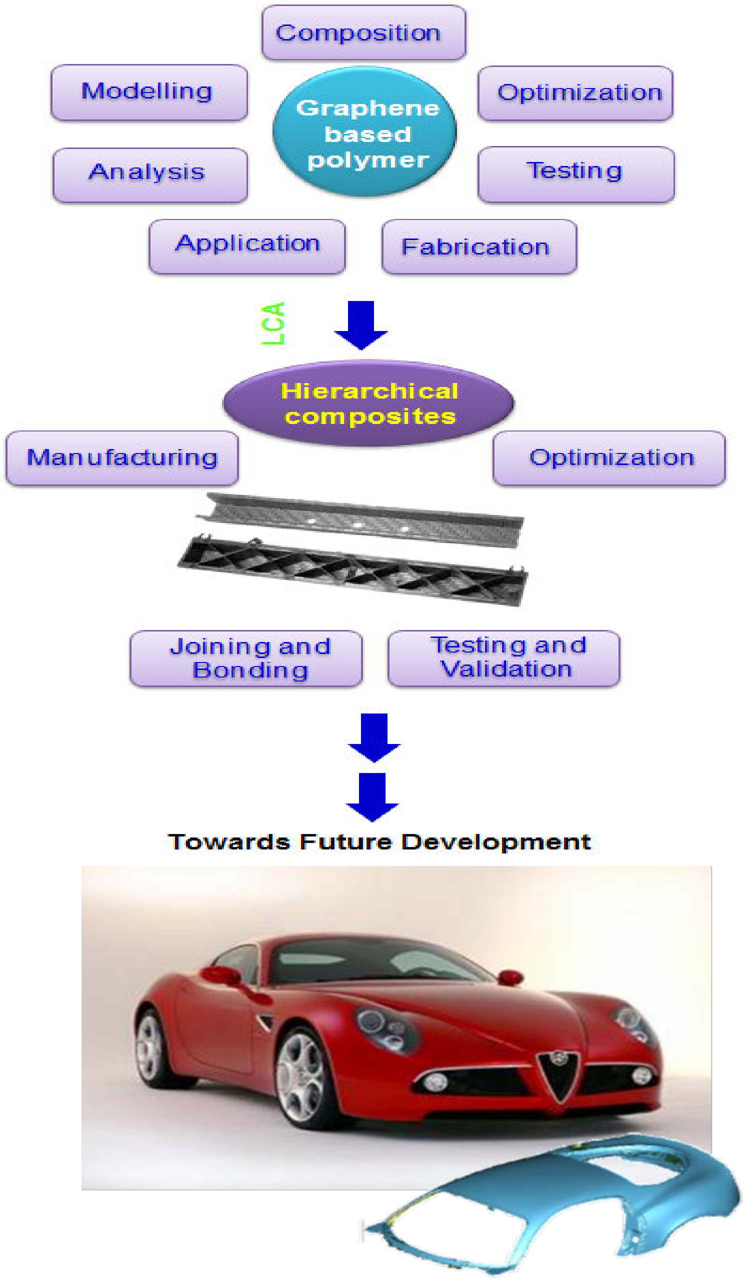

Figure 4: Graphene composites approach for automotive applications

- Development of a large scale-production method for graphene products based on high performance ultra-sonication systems. The process will have a low environmental impact and low operating and production costs without compromising the quality of the graphene. By varying the process parameters, this technology will allow to modify the morphological and geometric characteristics of the product, such as surface dimension and thickness, allowing customizing the type of graphene according to the final application;
- Development of methodologies for introducing graphene and functionalised graphene in different polymers;
- Delivering a level of industrial applicability readiness for various next generation graphene-based products materials tailored for automotive applications, which provide significant weight reduction as well as low intrinsic CO_2, a strong potential for part count reduction at an affordable cost level and without any negative impact on long term durability, static and dynamic performance, or crashworthiness;
- Development of reliable model of material behaviour. These describe how different components and their processing influence the microstructure of the composite material and its performance, allowing development of the material with an optimal behaviour during the processing steps;
- Development of advanced simulation capabilities with regard to the micro-mechanical behaviour of the materials addressed, which may exhibit unconventional failure mechanisms, specifically taking into account an-isotropic behaviour and optimisation of the new material and vehicle structural layouts;

4.3 Continues efforts

In addition to the above developments, more work to be carried out in this initiative to:

- understand the behaviour of these material systems in most suitable joining methods, and advancements in joining technologies towards realistic industrial solutions that can reliably and repetitively join a variety of materials: thermoplastics and thermoset composites, with full crash loading path functionality under all climate conditions and with full vehicle life reliability;
- Demonstrate the graphene-based composites in a simulacra representative of an automotive application. The project will produce and perform testing simulacra in order to validate the materials developed and their applicability in high-volume production scenarios;

- Develop high throughput manufacturing technologies for advanced lightweight graphene composite materials in order to bring costs down and achieve economic viability;
- Increase reliability in service and improved crashworthiness including protection of vulnerable road users through the application of the developed graphene-based composite materials and implementation of advanced energy absorption capabilities; enabling the application of next-generation materials in safety-critical parts;
- Develop thorough, well-quantified life cycle assessment (LCA) and economic analysis knowledge.

Besides, great efforts will be given to establish and develop a reliable material models and constitutive laws to investigate the energy absorption characteristics of new developed Graphene-based polymer composites. New combination of several modelling techniques will be considered including Molecular Models (i.e. Monte Carlo Simulations); Continuum Models (i.e. Eshelby Model, Mori-Tanaka, representative volume elements (RVE), and Halpin-Tsai Model); and then using smooth transition analysis considering combination of both meso-scale and multi-scale modelling.

The proposed constitutive law will be implemented in LS-DYNA finite element code as a user defined material subroutine (UMAT). The explicit nonlinear finite element code LS-DYNA will be used as an effective tool to numerically simulate the problem and to predict the effect of the crash load on the proposed composite materials and its components. The software has the ability to simulate dynamic structural response in several ways, including pure Lagrangian, and coupled Lagrange–Eulerian methods. This accurate and reliable numerical simulation does not exist in the market for initial design concept for automotive applications for such novel Graphene-based composite materials.

5 Place for graphene in the future of automotive industry

Graphene has tremendous applications for the automotive industry, and using it to enhance the composite materials in cars has considerable potential. As already highlighted in the above sections, the Graphene-based polymer composites are still in infancy stage with regard to high-performance structural applications. Working on the above challenges within the Graphene Flagship will guarantee a stable place for Graphene in the automotive sector. Our current work on Graphene Composites for Automotive advances innovative lightweight Graphene-based materials and their related modelling, designing, manufacturing, and joining capabilities suitable for automotive industry which requires unique levels of affordability, mechanical performance, green environmental impact and energy efficiency. It also revolutionises computer-based as well as experimental validation approaches (and their combinations) to allow for a fast, efficient and reliable development process. The effort is validated by means of a simulacra representative of an automotive application to be evaluated experimentally in combination with a full vehicle virtual design and simulation. This leads to complete understanding of the new Graphene composites and their applicability in high-volume production scenarios. We are expecting huge success for Graphene as a main player on developing composites for automotive applications.

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