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Review

The mechanics of graphene nanocomposites: A review

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ABSTRACT

The preparation and characterisation of the different forms of graphene are reviewed first of all. The different techniques that have been employed to prepare graphene such as mechanical and solution exfoliation, and chemical vapour deposition are discussed briefly. Methods of production of graphene oxide by the chemical oxidation of graphite are then described. The structure and mechanical properties of both graphene and graphene oxide are reviewed and it is shown that although graphene possesses superior mechanical properties, they both have high levels of stiffness and strength. It is demonstrated how Raman spectroscopy can be used to characterise the different forms of graphene and also follow the deformation of exfoliated graphene, with different numbers of layers, in model composite systems. It is shown that continuum mechanics can be employed to analyse the behaviour of these model composites and used to predict the minimum flake dimensions and optimum number of layers for good reinforcement. The preparation of bulk nanocomposites based upon graphene and graphene oxide is described finally and the properties of these materials reviewed. It is shown that good reinforcement is only found at relatively low levels of graphene loading and that, due to difficulties with obtaining good dispersions, challenges still remain in obtaining good mechanical properties for high volume fractions of reinforcement.

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1. Introduction

The study of graphene is one of the most exciting topics in materials science and condensed matter physics [1] and graphene has good prospects for applications in a number of different fields [2,3]. There has been a rapid rise of interest in the study of the structure and properties of graphene following the first report in 2004 of the preparation and isolation of single graphene layers in Manchester [4]. It had previously been thought that the isolation of single-layer graphene would not be possible since such 2D crystals would be unstable thermodynamically [5] and/or might roll up into scrolls if prepared as single atomic layers [6]. A large number of studies since 2004 have shown that this is certainly not the case. There was excitement about graphene initially because of its electronic properties, with its charge carriers exhibiting very high intrinsic mobility, having zero effective mass and being able to travel distances of microns at room temperature without being scattered [1,7]. Thus the majority of the original research upon graphene had concentrated upon electronic properties, aimed at applications such as using graphene in electronic devices [8,9].

Graphene is the basic building block of all graphitic forms of carbon. It consists of a single atomic layer of sp^2 hybridized carbon atoms arranged in a honeycomb structure as shown in Fig. 1. Research upon the material has now broadened considerably as it was soon realised that graphene might have other in interesting and exciting physical properties such as high levels of stiffness and strength, and thermal conductivity, combined with an impermeability to gases. One obvious application of graphene is in the field of nanocomposites [10–13] and researchers working upon other forms of nanocomposites, such as those reinforced by nanotubes or nanoclays, have now refocused their efforts towards graphene nanocomposites. Additionally there was pre-existing expertise in the exfoliation of graphite (e.g. expanded graphite) and in the preparation of graphene oxide (originally termed "graphite oxide"). We will also discuss the advantages and disadvantages of the use of graphene oxide in composite materials in comparison with pristine graphene.

2. Graphene

2.1. Preparation

There has already been considerable effort put into the development of ways of preparing high-quality graphene in large quantities for both research purposes and with a view to possible applications [14]. Since it was first isolated in 2004 several approaches have been employed to prepare the material. One is to break graphite down into graphene by techniques such as a mechanical cleavage or liquid phase exfoliation (sometimes termed "top-down"). The other methods is to synthesize graphene using techniques such as chemical vapour deposition (CVD) (often known as "bottom-up"), epitaxial growth on silicon carbide, molecular beam epitaxy, etc.

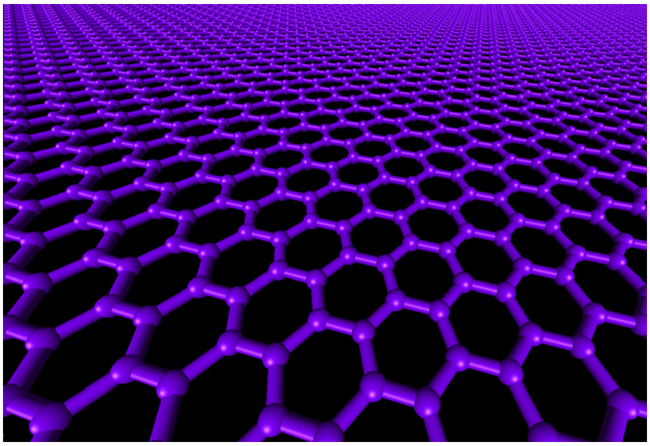

Fig. 1. A molecular model of a single layer of graphene. (Courtesy of F. Ding, Hong Kong Polytechnic University).

Expanded graphite was developed more than 100 years as a filler for the polymer resins that were being developed at the same time and investigated extensively over the intervening period [15,16]. More recently there have been developments in the preparation of thinner forms of graphite, known as graphite nanoplatelets (GNPs) [17]. They can be produced by a number of techniques that include the exposure of acid-intercalated graphite to microwave radiation, ball-milling and ultrasonication. The addition of GNPs to polymers has been found to lead to substantial improvements in mechanical and electrical properties at lower loadings than are needed with expanded graphite [18,19]. The definition of GNPs covers all types of graphitic material from 100 nm thick platelets down to single layer graphene [17]. It is, however, the availability of single- or few-layer graphene that has caused the most excitement in recent times.

The simplest way of preparing small samples of single- or few-layer graphene is by the mechanical cleavage (i.e. the repeated peeling of graphene layers with adhesive tape) from either highly-oriented pyrolytic graphite or good-quality natural graphite [4]. Typically, this method produces a mixture of one-, two- and many-layer graphene flakes that have dimensions of the order of tens of microns.

The rapid rise of interest in graphene for use in applications that require high volumes of material, such as in composites, led to investigations into methods of undertaking large-scale exfoliation [20–32]. One of the first successful methods was the exfoliation and dispersion of graphite in organic solvents such as dimethylformamide [20] or *N*-methylpyrrolidone [21–23]. Depending on the levels of agitation and purification suspensions with large (>50%) fractions of graphene monolayers could be prepared. The material produced by this method is relatively free of defects and is not oxidised but the lateral dimensions of the graphene layers are typically no more than a few microns. Coleman and coworkers [24,25] demonstrated that it was also possible to disperse and exfoliate graphite to give graphene suspensions in water-surfactant solutions and then showed that this approach could be extended to other inorganic layered compounds such as molybdenum disulphide, MoS_2 [26,27].

As well as producing graphene by exfoliation of graphite there are a number of way in which it can be grown directly using "bottom-up" methods. In the surface science literature there are a number of reports, that date back more than 40 years, claiming the preparation and observation of thin graphitic layers on metallic substrates, and Wintterlin and Bocquet [33] have recently reviewed the literature upon the formation of graphene on metal surfaces. In addition, epitaxial growth of thin graphitic films on silicon carbide has been known for some time [34].

An important breakthrough has been the growth graphene films with macroscopic dimensions on the surfaces of metals. Two general approaches have been developed; (i) the precipitation of carbon from a carbon rich metal such as nickel [35] and (ii) the CVD growth of carbon on copper [36] using methane/H_2 mixtures. Thick graphite crystals, rather than graphene, usually form on foils in the case of nickel and this problem has been overcome by depositing thin Ni layers of less than 300 nm on SiO_2/Si substrates [35]. In the case of copper, growth takes place upon Cu foils via a surface-catalysed process and thin metal films do not have to be employed [36–38]. For both metals, it was found that the graphene