



ELECTROMECHANICAL BEHAVIORS OF GRAPHENE REINFORCED POLYMER COMPOSITES: A REVIEW

Ms.Chanchal Lecturer ASH Department IIMT college of Polytechnic

Manju Gaur Lecturer ASH Department IIMT college of Polytechnic

Abstract

Carbon materials particularly in the form of sparkling diamonds have held mankind spellbound for centuries, and in its other forms, like coal and coke continue to serve mankind as a fuel material, like carbon black, carbon fibers, carbon nanofibers and carbon nanotubes meet requirements of reinforcing filler in several applications. All these various forms of carbon are possible because of the element's unique hybridization ability. Graphene (a single two-dimensional layer of carbon atoms bonded together in the hexagonal graphite lattice).

Introduction

Nanocomposites possess a large amount of interfaces due to the small (nanometer) size of reinforcements. The interface behavior can significantly affect the mechanical properties of nanocomposites. For example, carbon nanotubes in general do not bond well to polymers, and their interactions result mainly from the weak van der Waals forces. Consequently CNTs may slide inside the matrix and may not provide much reinforcing effect.

Depending on the number of concentrically rolled-up graphene sheets, CNTs are also classified to single-walled (SWNT), double-walled (DWNT), and multiwall CNTs (MWNT). The structure of SWNT can be conceptualized by wrapping a one-atom-thick layer of graphene into a seamless cylinder. MWNT consists of two or more numbers of rolled-up concentric layers of graphene. DWNT is considered as a special type of MWNT where in only two concentrically rolled up graphene sheets are present. There are two models to describe the structures of MWNT. CNT made from graphene sheet zigzag and armchair.

Man has also created several other forms of carbon (engineered carbons) and some of these are: synthetic graphite and synthetic diamonds, adsorbent carbon, cokes, carbon black, carbon and graphitic fibers, glassy carbons, diamond-like carbon, etc., for application in various end uses like electrodes and electrical contacts, lubricants, shoe polish, gemstones, cutting wheels, gas adsorption, catalytic support, helium gas barrier, tire and elastomer reinforcement, toner for photocopying machines and printing inks, high performance tennis rackets, aircraft and spacecraft composites, heat sinks for ultrafast semiconductors, etc.. All these various carbon forms can be ascribed to carbon's unique hybridization properties. The ground state orbital configuration of carbon is $1s^2 2s^2 2p^2$.

In this review we provide a brief introduction to graphite, discuss its structure and properties, the various modifications studied till date solely for applications targeted as modified filler in polymeric nanocomposites and culminate with an anthology of the different processing methodologies explored till date. In graphite, elemental carbon has the lowest energy state at ambient temperature and pressure. The graphite crystal lattice consists of stacks of parallel two-dimensional (2D) graphene sheets (a single carbon layer in the crystalline honeycomb graphite lattice is known as a graphene layer or graphene sheet) with sp^2 hybridized carbon atoms tightly bonded in hexagonal rings. Since the $2p_z$ orbitals of the carbon atoms can overlap most effectively if they are parallel (out-of-plane bond), the graphene sheet has lowest energy when it is completely flat. Thus, graphite is anisotropic due to the difference between in-plane and out-of-plane bonding of the carbon atoms. The elastic modulus is higher parallel to the plane than it is perpendicular to the plane and in this respect graphite is stronger in plane than diamond. The p_z orbital is distributed over the entire graphene sheet making it thermally and electrically conductive.



A composite material can be defined as a combination of two or more materials that results in better properties than those of the individual components used alone. In contrast to metallic alloys, each material retains its separate chemical, physical, and mechanical properties. The two constituents are reinforcement and a matrix. The main advantages of composite materials are their high strength and stiffness, combined with low density, when compared with bulk materials, allowing for a weight reduction in the finished part.

The reinforcing phase provides the strength and stiffness. In most cases, the reinforcement is harder, stronger, and stiffer than the matrix. The reinforcement is usually a fiber or a particulate. Particulate composites have dimensions that are approximately equal in all directions. They may be spherical, platelets, or any other regular or irregular geometry. Particulate composites tend to be much weaker and less stiff than continuous fiber composites, but they are usually much less expensive. Particulate reinforced composites usually contain less reinforcement (up to 40 to 50 volume percent) due to processing difficulties and brittleness

2. Modifications of graphite

In its bulk state, graphite exists as a layered material. For the efficient utilization of graphite as a filler in a polymer composite, its layers must be separated and dispersed throughout the polymeric matrix. Graphite nanoplatelet (GNP), the basic unit obtained by exfoliation of the natural flaky graphite and having a platelet thickness varying from less than 0.34 to 100 nm, is a promising low cost and lightweight alternative to metal- and carbon-based electrically conducting reinforcements for conducting polymer composites [18,28–36]. Graphite does not bear any net charge and thus is different from silicate clay minerals. In its natural form, no reactive ion groups exist on the graphene layers and as a result, it is impossible to intercalate monomers into the graphite galleries by ion exchange reactions as is possible for the layered silicates. However, graphite is readily intercalated and can host various atoms, molecules, metal complexes and salts between the expanded graphene sheets to form graphite intercalation compounds (GICs). So far, GNPs are mainly obtained from sulfuric acid-intercalated graphite and graphene oxide (GO).

2.1. Graphene oxide (GO)

Because of expensive and hard to synthesize the graphene, needs to find inexpensive ways to produce graphene derivatives such as graphene oxide. From the cheap and abundant quantity of graphite, it was obtained as single-atomic layered material. Graphene oxide is a form of graphene decorated with oxygen-containing groups. When compared to graphene, GO is easily dispersible in water as well as any other solvents. It is easy to process and also make graphene too. The starting material for several electronic devices such as graphene-based field effect transistor is GO [42]. Effective way to synthesize graphene is chemical reduction of GO. GO is obtained by exfoliating graphite oxide through sonication. Chemical reduction of GO is currently seen as the most suitable method of mass production of graphene.

2.2. Graphite intercalation compounds (GICs)

Graphite intercalation compounds (GICs) have a variety of functions due to their rich material variations, and thus, innovative methods for their synthesis are desired for practical applications. It is discovered that Na has a catalytic property that dramatically accelerates the formation of GICs. It is demonstrated that LiC_{6n} ($n = 1, 2$), KC_8 , KC_{12n} ($n = 2, 3, 4$), and NaC_x are synthesized simply by mixing alkali metals and graphite powder with Na at room temperature ($\approx 25^\circ\text{C}$), and A_EC_6 ($\text{A}_E = \text{Ca}, \text{Sr}, \text{Ba}$) are synthesized by heating Na-added reagents at 250°C only for a few hours. The NaC_x , formed by the mixing of C and Na, is understood to act as a reaction intermediate for a catalyst, thereby accelerating the formation of GICs by lowering the activation energy of intercalation. The Na-catalyzed method, which enables the rapid and mass synthesis of homogeneous GIC samples in a significantly simpler manner than conventional methods, is anticipated to stimulate research and development for GIC applications



2.3. Expanded graphite (EG)

In this study, expanded graphite (EG) was added to melted stearic acid (SA) by the melt blending method to prepare SA/EG composite phase change material (PCM) with different ratios. EG with ultra-high porosity and large specific surface area can effectively adsorb melted SA through capillary force and van der Waals force. The results showed that when the loading amount of EG was 12 wt.%, almost no liquid leakage occurred and the composite showed excellent stability. In addition, the three-dimensional network structure of EG interconnection provides an efficient heat transfer path and reduces the thermal resistance of the interface. Therefore, the thermal conductivity of the composite was as high as $6.54 \text{ W m}^{-1} \text{ K}^{-1}$, which was 19.179 times higher than that of pure SA. Furthermore, the melting enthalpy and melting temperature of the composite were 163.35 J g^{-1} and $67.08 \text{ }^\circ\text{C}$, respectively. X-ray diffraction and Fourier transform infrared spectroscopy shown that physical interaction instead of chemical reaction happened between EG and SA. When the mass fraction of EG is 12 wt.%, the composite PCM shows a relatively more balanced and uniform thermal image compared with SA, and the heat storage rate of the composite PCM was about 2.3 times of SA, and the heat release rate was 3.1 times of SA. In addition, the composite PCM showed excellent thermal stability, chemical stability, and cyclic stability, indicating that the working performance of the composite PCM was relatively stable within the temperature range of $100 \text{ }^\circ\text{C}$.

2.4. Graphene

Graphene is a material that is extracted from graphite and is made up of pure carbon, one of the most important elements in nature and which we find in daily objects like the lead of a pencil. Graphene stands out for being tough, flexible, light, and with a high resistance.

3. Methods of manufacturing polymer/graphite nanocomposites

3.1 Electrospinning Technique

Electrospinning has been considered as a sophisticated manufacturing technique for polymeric nanocomposites. The material is generally produced in the form of nanofibers. Graphene-filled polymeric nanocomposite nanofibers have been produced using electrospinning. The electrospinning has been carried out using a set-up with a syringe with polymer/graphene dispersion, a spinneret, a collector, and a high-voltage system. During nanofiber spinning, the polymer solution is fed into a syringe with a needle. The polymer solution ejected from the needle forms a fiber jet under an applied voltage. Due to the electrostatic driving force, the nanofibers move to the spinneret and collector. Due to the electrostatic field, fine nanofibers have been generated using various materials. The electrospinning parameters have been adjusted to better regulate the resulting electrospun fiber texture, microstructure, and physical characteristics. The electrospun polymer/graphene nanofibers have upgraded electrical, thermal, and mechanical properties, relative to neat polymer nanofibers and non-electrospun nanocomposites. Transmission electron microscopy and scanning electron microscopy have been mostly adopted to study the nanofiber morphology. Consequently, the electrospinning technique has been predictable as a fast and competent method for manufacturing polymer/graphene nanofibers.

3.2. Melt blending

Melt blending is the preferred method for preparing clay/polymer nanocomposites of a thermoplastics and elastomeric polymeric matrix [28]. Typically, the polymer is melted and combined with the desired amount of the intercalated clay using banbury or an extruder. Melt blending is carried out in the presence of an inert gas, such as argon, nitrogen, or neon. Alternatively, the polymer may be dry mixed with the intercalant, then heated in a mixer and subject to shear sufficient to form the desired clay polymer nanocomposites. Melt blending has great advantages over in situ intercalative polymerization or polymer solution intercalation. Melt blending is environmentally benign due to the absence of organic solvents. Melt blending is compatible with current industrial processes, such as extrusion and injection molding. Due to its potential in industrial applications, the melt blending process has become popular.



3.3 Combination of mixing techniques

The tensile and electrical properties of various polymer/graphite composites prepared by a combination of in situ polymerization, solution compounding with one or more of the following procedures: melt blending, shear mixing, masterbatch blending, etc. This combinatorial approach involving various techniques becomes necessary when the system viscosity increases rapidly with solvent decrease as in the case of epoxy matrices. For proper filler dispersion in various polymeric systems, this combinatorial approach has been adopted by several authors. This is a promising approach, as it can mitigate the problems faced in each of the individual techniques.

4. General conclusions and remarks

The development of graphitic fillers derived from natural graphite which is inexpensive and available in large quantities (worldwide reserves estimated at 800 million metric tons), has opened up a new vista in the field of materials science for developing a wide range of novel functional materials. CNTs had afforded higher Young's modulus and tensile strength than all the other existing fillers, but with the advent of graphene, a 2D wonder material, the scenario has changed. Graphene, CMG and FGS appear to be cutting edge materials with which the electrical conductivity, stiffness and strength, barrier resistance, fire retardancy, thermal properties and piezoelectric properties of polymeric nanocomposites can be tailored according to requirement at very low carbon content. Various processing techniques such as SC, ISP, MB, SSSP, pan milling and masterbatch melt mixing have been used for the preparation of graphite-based polymer nanocomposites and are discussed here. Finally, the benefits of combinatorial mixing techniques have been illustrated to indicate the path ahead. Today, EG and GO have been recognized as the obvious intermediates for the preparation of GNPs.

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