Chapter 1

Introduction

Introduction

Among all the polymeric materials, elastomers are unique and have been studied extensively in both fundamental and applied research fields owing to their advantages of easy processing, remarkable flexibility, corrosion resistance and excellent thermal properties.^{1–2} The reversible deformability of elastomers is of great industrial importance. Typically, however, the initial modulus and strength of such materials are low, and an additional reinforcing phase is required for practical use. Conventionally, carbon black, silica etc are used as reinforcing fillers for elastomers.^{3–7} The extent of improvement of properties depends on several parameters including the size of the particles, their aspect ratio, their degree of dispersion and orientation in the matrix and the degree of adhesion with the polymer chains.⁸ For the composite to be effective, there must be a strong interaction between the matrix and the stiffer phase. This can be achieved using filler with a large surface area-to-volume ratio. In order to create new material systems with superior properties, various nanoparticles have been used as reinforcing fillers in elastomeric matrices. These nanometer scale reinforcing particles include spherical particles such as silica, titania or zinc oxide,⁹⁻¹² platelets such as layered silicates and graphites,¹³⁻²¹ and single walled or multiwalled carbon nanotubes (SWCNTs or MWCNTs).^{22–28}

1.1 Types of Nanofillers

Various kinds of nanofillers (both organic and inorganic) are used in the development of polymer based nanocomposites.

Nanofillers can have different shapes:

- Spherical [e.g., nanosilica, polyhedral oligomeric silsesquioxanes (POSS)]
- Sheet / platelet (e.g., graphites, layered silicates, synthetic mica etc.).
- Rod / fiber (e.g., carbon nanotubes (CNTs), carbon nanofibers (CNFs), synthetic whiskers etc.)

These fillers have also different surface chemistry. For example, graphite is quite inert as compared to silica, which has a large number of silicate groups. Various research groups

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have worked on the development of polymer nanocomposites based on these nanofillers. Several studies have been carried out on clay nanocomposites based on natural as well as synthetic rubbers.^{29–37} Nanodimensional silica, POSS and zinc oxide were also used by many researchers for the development of nanocomposites.^{38–40}

. Among the nanofillers, carbon based nanofillers hold a special interest since various polymeric matrices are proved to be very compatible for carbon based fillers.^{41–48} Several applications of polymers might benefit from inclusion of CNTs, CNFs and expanded graphites (EG), to form polymer based nanocomposites. In this thesis, carbon based nanofillers have been used as reinforcing agents. Hence, detailed discussion on these fillers is given below.

1.1.1 Graphites

Graphite is an allotrope of carbon, the structure of which consists of graphene layers stacked along the c-axis in a staggered array.⁴⁹ In a graphene sheet, each carbon atom forms bonds with three other carbon atoms to produce a two-dimensional honeycomb structure (Fig. 1.1). These carbon-carbon bonds are very strong, which renders graphene stable, even when it has been cut into nanoscale structures.



Fig. 1.1: Honeycomb Layer Structure of Graphite

High crystallinity of graphite is disadvantageous in forming the nanocomposites with polymers, as the giant polymer molecules do not find spaces within the graphene sheets. This has been overtaken by modifying the graphite flakes with several oxidizing agents.⁵⁰ The effective method of preparing the polymer/expanded graphite composite is by rapidly heating the pre-treated (oxidized) graphite to a high temperature. The exfoliation of graphite is a process in which graphite expands several times along the c-axis, resulting in a puffed-up material with a low density and a high temperature resistance.⁵¹ Expanded graphites exhibit a layered structure similar to layered silicates. An exfoliated graphite nanoparticle is composed of stacks of nanosheets that may vary from 4 to 40 nm. Graphite is also well known for its stiffness, light weight, excellent thermal conductivity, heat resistance, and is known to be a good solid lubricant and pencil material corresponding to its structural anisotropy.

1.1.2 Carbon Nanotubes

CNTs are often seen as the intersection of traditional carbon fibers with the fullerene family.⁵² It is only realized relatively recently that solids of pure elemental carbon with sp^2 -hybridization can form a wide variety of well-defined crystalline structures. The first recognition of the fullerenes as closed structures ⁵³ in 1985, and their subsequent synthesis in a carbon arc ⁵⁴ has stimulated enormous new interest in carbon materials. In 1991, Iijima has observed a graphitic tubular structure in an arc discharge apparatus that has been used to produce C_{60} and other fullerenes. His realization of the structural richness of these particles, which came to be known as nanotubes, generated enormous interest.⁵⁵

CNT is a hexagonal network of carbon atoms rolled up into a seamless, hollow cylinder, with each end capped with half of a fullerene molecule.⁵⁶ Although similar in chemical composition to graphite, CNTs are highly isotropic, and it is this topology that distinguishes them from other carbon structures and gives them their unique properties. There are many possibilities for rolling a slice of graphene into a seamless cylinder,⁵⁷ because when rolled into a nanotube, the hexagons may spiral around the cylinder, giving rise to "chirality," a twist that determines whether the CNT behaves like a metal or a semiconductor. The various ways of rolling graphene into tubes are described by the tube

chirality (or helicity or wrapping) as defined by the circumferential vector, $C_h = na_1 + ma_2$ (Fig. 1.2), where the integers (n, m) are the number of steps along the unit vectors (a_1 and a_2) of the hexagonal lattice.^{58, 59} The parameters a_1 and a_2 are the primitive lattice vectors of the hexagonal lattice. The position and length of the vector, connecting an origin to the lattice point that defines the nanotube index, determine the helicity and diameter of the tube.⁶⁰ Using this (n, m) naming scheme, the three types of orientation of the carbon atoms around the nanotube circumference are specified as armchair (n = m), zigzag (n = 0 or m = 0), or chiral (all others). The chirality of nanotubes has significant impact on its transport properties, particularly the electronic properties.^{61, 62}



Fig. 1.2: CNT- Possible Conformations

CNT can be single walled or multiwalled depending on the number of graphitic cylinders with which it is formed. SWCNT and MWCNT generally exist with diameter of 1–2 nm and 10–40 nm respectively with a length of few micrometers.

CNTs are generally produced by three main techniques- arc discharge, laser ablation and chemical vapour deposition (CVD).²⁵ In arc discharge, a vapour is created by an arc discharge between two carbon electrodes with or without catalyst. Nanotubes self-assemble from the resulting carbon vapour. In the laser ablation technique, a high-power laser beam impinges on a volume of carbon containing feedstock gas (methane or carbon monoxide). CVD synthesis is achieved by putting a carbon source in the gas

phase and using an energy source, such as plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. Commonly used gaseous carbon sources include methane, carbon monoxide and acetylene. The energy source is used to "crack" the molecule into reactive atomic carbon. Then, the carbon diffuses towards the substrate, which is heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it will bind. Excellent alignment as well as positional control on nanometer scale, can be achieved by using CVD. Control over the diameter as well as the growth rate of the nanotubes can also be maintained. At present, laser ablation produces a small amount of clean nanotubes, whereas arc discharge methods generally produce large quantities of impure material. In general, CVD results in MWCNT or poor quality SWCNT. The SWCNTs produced with CVD have a large diameter range, which can be poorly controlled. But on the other hand, this method is very easy to scale up, what favours commercial production. Since their discovery in 1991,⁵⁵ CNTs have attracted enormous attention for their fundamental behavior and for their use in a wide variety of applications in nanoelectronic devices ^{63–65}, probe tips for scanning probe microscopes ⁶⁶, ⁶⁷ or in the automotive and aerospace industries for the dissipation of electrostatic charges.^{68, 69} The nanosize, aspect ratio and the properties of CNTs provide advantages in diverse applications, such as electrostatically dissipative materials; advanced materials with combined stiffness, strength and impact for aerospace or sporting goods, probe tips for atomic force microscopy imaging applications.^{28, 70, 71}

1.1.3 Carbon Nanofibers

CNFs are grown most efficiently from nanoscale metal catalyst particles (iron, nickel) exposed to a carbon-containing feedstock at high temperature ^{72–75} (Fig. 1.3). Carbon is absorbed on to the particle and then participates to form a highly graphitic strand with a diameter somewhat larger than the catalyst particle. A CNF generally can be composed of two phases of carbon, designated as the "catalyst" phase and the "deposited" phase. The catalyst phase is that which is formed by the catalytic action of the metal seed particle from which the CNF grows. This phase tends to be highly graphitic. The deposited phase is formed by CVD of carbon on top of the catalyst phase. The CVD carbon tends to be disordered (turbostratic) unless subjected to high

temperature, which tends to graphitize the carbon. CNFs are mainly differentiated from nanotubes by the orientation of the graphene planes: whereas the graphitic layers are parallel to the axis in nanotubes, nanofibers can show a wide range of orientations of the graphitic layers with respect to the fiber axis. They can be visualized as stacked graphitic discs or (truncated) cones, and are intrinsically less perfect as they have graphitic edge terminations on their surface. Nevertheless, these nanostructures can be in the form of hollow tubes with an outer diameter as small as ~5 nm, although 70-200 nm is more typical. The stacked cone geometry is often called a 'herringbone fiber' due to the appearance of longitudinal cross-section. Unlike in CNTs, the graphene layers in CNFs are at some angle with the fiber axis, whereas in CNTs these lie parallel to the fiber axis. Also, the CNFs are more defective, whereas the CNTs are highly crystallized tubular structures.⁷⁶ CNFs can be very inexpensive due to their size and the use of natural gas as the source of hydrocarbon gas.⁷⁷ The graphitic platelets are precipitated parallel to the faceted catalyst particle, and hence the angle between the planes and the fiber axis is determined by the shape of the catalyst particle.⁷⁸ Under certain conditions of gas composition, temperature and catalyst composition, the catalyst particles undergo surface reconstruction to form unique geometrical shapes which drive the formation of CNFs.⁷⁹





Difference Among Various Carbon Nanostructures

Buckyballs, nanotubes and nanofibers form a continuum of carbon nanomaterials. Buckyballs are single fullerene molecules of carbon, such as C_{60} , C_{70} , etc. SWCNTs are effectively the cylindrical version of buckyballs - a tube of carbon atoms with a diameter equal to that of a corresponding spherical buckyball, and which may have buckyball hemispheres as end caps. Some nanotubes are formed by a process that involves growth from a metal catalyst particle. In some cases, particularly smaller diameter nanotubes, the catalyst particle is thought to dance around the end of the nanotube, adding carbon atoms to the structure as it goes. In larger nanotubes, the catalyst particle remains static at the end of the tube, and adds to the entire rim of the cylinder at once, and a MWCNT is usually formed. For smaller nanotubes, the allowed diameters are determined by the energetics of the curved carbon structure. For the larger nanotubes, the diameter of the core), the number of layers of catalytically grown carbon (which sets the outer diameter of the core), and the amount of extra vapour deposited carbon that may form on them (which sets the final total diameter). These larger structures (~ 70- 200 nm) are termed as nanofibers. Once a nanofiber is formed, it is possible to increase its diameter, through chemical vapor deposition, to the diameter of conventional carbon fibers.⁸⁰

A variety of synthesis methods now exists to produce carbon nanotubes and nanofibers. However, these carbon nanostructures differ greatly with regard to their diameter, aspect ratio, crystallinity, crystalline orientation, purity, entanglement, surface chemistry and straightness. These structural variations dramatically affect intrinsic properties, processing, and behaviour in composite systems. However, it is not yet clear which type of nanotube material is most suitable for composite applications, nor is there much theoretical basis for rational design. Ultimately, the selection will depend on the matrix material, processing technology, and the property enhancement required.⁸¹

1.2 Surface Modification of Carbon Nanofillers

Since natural graphite as such is not reinforcing, it is subjected to various modifications to disperse it in the nanometer range within a polymer matrix. Various kinds of modification include high temperature expansion to produce expanded graphite with a thickness of few nanometers or oxidizing the natural graphite in order to induce polarity on the surface. The development and various characterizations of expanded graphite and graphite oxide have been reported by many scientists.^{50, 82–86}

An enhancement of the compatibility to the composite material could be achieved by a chemical functionalization of the nanotube surface, through covalent or ionic bonds to a polymeric matrix. These bonds enable stress transfer between polymer and CNT, which leads to improved interfacial interactions.^{87, 88}

The CNF surface has a significant fraction of layer edge defects due to the presence of tilted graphite layers with respect to the CNF axis.⁸⁹ These defects favour the attachment of chemical functional groups on to CNF surface. CNFs modified by plasma exhibit a great number of reactive groups on the surface, improving the compatibility with a polymer matrix.^{90–93}

1.3 Polymer Nanocomposites

1.3.1 Definition of Nanocomposites

The term, 'nanocomposite' refers to every type of materials having fillers in the nanometer size range at least in one dimension.^{18, 94–99} The concept of creating both structural and functional multi-phase nanocomposites with improved performance is currently under development in a wide variety of metallic, ceramic, and polymeric matrices, although the emphasis to date has been on polymeric systems. Similarly, the filler particles can be organic or inorganic with a wide range of material compositions and structures. The resulting composites generally exhibit a number of enhanced properties. Crucial parameters in determining the effect of fillers on the properties of composites are the filler size, shape, aspect ratio and the filler-matrix interactions.

In this thesis, carbon nanofillers- ethylene vinyl acetate (EVA) nanocomposites are discussed, where the nanofillers Expanded graphite (EG), MWCNT and CNF have their thickness or diameter in the nanometer range.

1.3.2 Nanocomposites vs. Traditional Filled Polymers

Nanocomposites can show excellent properties at very low filler loadings. Nanofillers are necessarily nanoscopic and have a high specific surface area. The specific surface area is one of the reasons why the nature of reinforcement is different in