



A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites

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ABSTRACT

Carbon materials particularly in the form of sparkling diamonds have held mankind spell-bound 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),

Abbreviations: 100% modulus, modulus at 100% elongation (MPa); 300% modulus, modulus at 300% elongation (MPa); 2D, two-dimensional; ABS, acrylonitrile–butadiene–styrene terpolymer; a-PP, atactic polypropylene; AS, acrylonitrile–styrene resin; ATRP, atom transfer radical polymerization; Br-GNP, bromine doped GNP; CB, carbon black; CCB, conducting carbon black; CMG, chemically modified graphene; CNT, carbon nanotube; CNT-MA-PP, polypropylene-wrapped carbon nanotubes via maleic anhydride grafting; CPAN, conjugated polyacrylonitrile; DMF, dimethyl formamide; EB, elongation at break (%); EG, expanded graphite; EG-g-PS, expanded graphite grafted with polystyrene; EM, electromagnetic; EPDM, ethylene propylene diene monomer; ER, electrical resistivity (Ω cm); EVA, ethylene-co-vinyl acetate; FG, foliated graphite (EG in which the worm-like structure has been broken into separated platelets); FGS, functionalized graphene sheets; FM, flexural modulus (GPa); FS, flexural strength (MPa); f-SWNT, functionalized single walled carbon nanotube; G_{IC} , fracture energy ($J m^{-2}$); GIC, graphite intercalated compound; GO, graphene oxide; GNP, graphite nanoplatelet; HDPE, high density polyethylene; HFFR, halogen free flame retardant; HIPS, high impact polystyrene; IIS, Izod impact strength (J/m); iPP, isotactic polypropylene; ISP, in situ polymerization; KB, ketjenblack (nanosized high structure carbon black); KC_{48} , stage IV K-GIC compound; K_{IC} , mode I fracture toughness ($Pa m^{-2}$); K-THF-GIC, potassium–tetrahydrofuran–graphite intercalation compound; LC, latex compounding; LCVG, liquid cooling and ventilation garment; LLDPE, linear low density polyethylene; MA-g-PE, maleic anhydride grafted polyethylene; MA-g-PP, maleic anhydride grafted polypropylene; MAI, macroazoinitiator; MAI-GO, GO intercalated with macroazoinitiator; MB, melt blending; MBFP, master batch filling process; MEG, modified expanded graphite; MEMS, micro-electro-mechanical systems; MMA, methyl methacrylate; MMB, masterbatch melt blending; MPEO, poly(ethylene oxide) methyl ether; MWNT, multi walled carbon nanotube; NBR, acrylonitrile–butadiene rubber; NCIS, notched Charpy impact strength (J/m^2); NCO, isocyanate group; NTC, negative temperature coefficient; ODA-MMT, octadecylamine modified montmorillonite; PA6, polyamide 6; PAN, polyacrylonitrile; PAN-CF, PAN based carbon fiber; PAS, poly(arylene sulfide); PC, polycarbonate; PE, polyethylene; PEFC, polymer electrolyte fuel cell; PEN, poly(ethylene-2,6-naphthalate); PEO, poly(ethylene oxide); PETI, phenylethynyl-terminated polyimide; phr, parts per hundred parts rubber; PMMA, poly(methyl methacrylate); POBDS, poly(4,4'-oxybis(benzene)disulfide); POM, polyoxymethylene; PPEn, poly(phenylene ethynylene); PP, polypropylene; PPCR, positive pressure coefficient of resistivity; PPCP, propylene ethylene random copolymer; PPE, poly(phenylene ether); PPS, poly(phenylene sulfide); PS, polystyrene; PT, percolation threshold; PTC, positive temperature coefficient; PU, polyurethane; PVC, polyvinyl chloride; PVDF, poly(vinylidene fluoride); RPUF, rigid polyurethane foam; RTC, room temperature conductivity (S/cm); RTV, room temperature vulcanization; SAN, poly(styrene-co-acrylonitrile); SBR, styrene–butadiene rubber; SC, solution compounding; SGN, sulfur/graphite nanocomposite; SR, silicone rubber; SMI, solid state pan milling intercalation; SSSP, solid state shear pulverization; SWNT, single walled carbon nanotube; TC, thermal conductivity ($W m^{-1} K^{-1}$); TD, thermal diffusivity (m^2/s); THF, tetrahydrofuran; TPU, thermoplastic polyurethane; TPV, thermoplastic vulcanizate; TRGO, thermally reduced graphene oxide; TS, tensile strength (MPa); UG, natural unmodified graphite; UPR, unsaturated polyester resin; UTS, ultimate tensile strength (MPa); UV/O_3 , ultraviolet and ozone treatment; VGCNF, vapor grown carbon nanofiber; xGNP, exfoliated GNP; Y, Young's modulus (GPa).

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the basic building block of graphite, is at the epicenter of present-day materials research because of its high values of Young's modulus, fracture strength, thermal conductivity, specific surface area and fascinating transport phenomena leading to its use in multifarious applications like energy storage materials, liquid crystal devices, mechanical resonators and polymer composites. In this review, we focus on graphite and describe its various modifications for use as modified fillers in polymer matrices for creating polymer–carbon nanocomposites.

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1. Introduction

Carbon, the sixth element in the Periodic Table of Elements, is truly remarkable for its extraordinary ability of catenation to combine with itself and other chemical elements in different ways and thereby form the basis of organic chemistry and of life. In nature, it is abundantly available as coal or as natural graphite, and in lesser quantities as diamonds. Diamond and graphite, the well-known allotropes of carbon have now been joined by fullerenes (C₆₀, C₇₀) [1,2], fullerene-related materials (like carbon onions) [3], carbon nanofibers [4,5] and also carbon nanotubes [6–8]—all of which are carbon based nanomaterials. The study of carbon nanostructures became very important with the discovery of fullerenes in 1985 [9] and carbon nanotubes in 1991 [10]. This is due to the fact that fullerenes serve as prototypes for zero-dimensional quantum dots while nanotubes serve as prototypes for one-dimensional (1D) quantum wires [7].

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. [11–13]. All these various carbon forms can be ascribed to carbon's unique hybridization properties. The ground state orbital configuration of carbon is 1s² 2s² 2p². The narrow

energy gap between the 2s and 2p orbitals facilitates the promotion of one 2s electron to a vacant higher energy 2p orbital. This electron promotion allows carbon to hybridize into sp, sp² and sp³ configurations leading to fascinating and diverse molecular structures. The sp bonding gives rise to chain structures, sp² bonding gives rise to planar structures and sp³ bonding to tetrahedral structures. The hybridization states of some typical carbon nanomaterials are summarized in Fig. 1.

In this era of nanocomposites research, a lot of emphasis has been directed towards the study of carbon based nanofillers mostly carbon nanotubes (CNTs) and to a limited extent to graphite and vapor grown carbon nanofibers (VGCNFs). However, the use of CNTs in nanocomposites to date has been limited by challenges in processing and dispersion, but the biggest hurdle for extensive use is their exorbitant price. Multiwall carbon nanotubes (MWNTs) are priced at ~\$8/g, single wall carbon nanotubes (SWNTs) cost ~\$170/g and graphite nanoplatelets are priced at ~\$2/kg [14]. As a matter of fact, from a geometric perspective (Fig. 2), carbon nanostructures like CNTs and VGCNFs can be obtained by the coiling up of the covalent graphene building units resulting in a three dimensional structure [15].

Several excellent reviews are available which specifically deal with graphene [16], chemical methods for

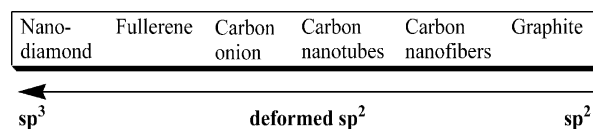


Fig. 1. Hybridization states of some typical carbon nanomaterials.

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