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Review

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A review of electrically conductive poly(ether ether ketone) materials

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Abstract

Poly(ether ether ketone) (PEEK) is a high-performance thermoplastic with a distinctive combination of corrosion resistance, thermo-oxidative stability and outstanding physical and mechanical properties at high temperatures. A pertinent step forward in the development of this thermoplastic has been the inclusion of electrically conductive fillers to expand its functionality. In this review an overview of the research on electrically conductive PEEK composites is provided. Conductive filler type, fabrication methods, characterization details and different properties are described. Carbon nanotubes, graphene nanoplatelets and other organic and inorganic conductive fillers such as expanded graphite and nickel have been incorporated into PEEK by techniques such as extrusion, injection moulding and cold and hot compression moulding and in some cases with pre-processing steps including mechanochemical modifications in organic solvents. The influences of type, loading and compatibilization of fillers and processing conditions on the mechanical and electrical conductivity properties of the composites are analysed and compared. The incorporated fillers have been able to enhance the electrical conductivity of the PEEK composites to either the semiconducting or conductive regions. PEEK composites containing carbon nanotubes compatibilized by polysulfones and poly(ether imide) achieved electrical conductivity values in the semiconducting region at the lowest electrical percolation threshold of 0.1 wt%. Additionally, the inclusion of 10 wt% expanded graphite and 10 vol% inorganic macroparticles of nickel noticeably improved the electrical conductivity of PEEK into the conductive region.

Keywords: PEEK; electrical conductivity; conductive fillers; high performance

INTRODUCTION

The first effort to synthesize PEEK occurred in 1967 and Victrex PEEK was commercialized by Imperial Chemical Industries in 1982.[1–3] PEEK is a thermoplastic with exceptionally high melting and glass transition temperatures due to its crystallinity and its stiff backbone interconnected by ketone and ether groups. It can be moulded by injection moulding and is used in nuclear plants, military, aerospace, chemical process equipment, oil-well and bio applications.[4–10] PEEK has wide commercial application in electronic, telecommunication, healthcare and transportation industries (automotive, aeronautics and aerospace) and interest is continually growing in the ability to manufacture PEEK composites for electromagnetic interface (EMI) shielding and anti-static applications to further enhance its applicability in these sectors.[11–18] Greater specific strength, more efficient, sustainable and cost effective mass production, higher corrosion resistance, and the absorption-based mechanism of EMI shielding of PEEK materials has given rise to significant interest in PEEK as a replacement for metals from industries such as aerospace, weapons and microelectronics.[19–23] Many studies have been carried out to improve the electrical conductivity of PEEK mostly by incorporating carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) using solution mixing and melt blending.[24–27] Díez-Pascual *et al.*[12,28–30] obtained high-performance PEEK composites with very low electrical percolation threshold by including polysulfone and poly(ether imide) (PEI) compatibilized multi-walled CNTs (MWCNTs) into PEEK. Yang *et al.*[31] added thermally reduced graphene nanosheets modified by poly(ether sulfone) (PES) into PEEK and this produced an abrupt transition from electrical insulator to semiconductor behaviour at 1 wt%. Electrically conductive PEEK composites, like other conductive polymer composites, have different electrical percolation thresholds due to differences in parameters such as type and grade of nano-filler, modification of the surface chemistry of the nano-filler and the type and quality of mixing, which will be discussed in detail in the next sections.[32–40] In a few studies, other fillers such as Ag nanoparticles (AgNPs) and nanowires (AgNWs), Ni macroparticles and expanded graphite (EG) were loaded into PEEK to improve its electrical conductivity.[41–45] Also, other methods such as surface metallization has been applied by Zhai et al[46] on the surface of electrically conductive PEEK/MWCNT composites to reduce the difference between the volume and surface resistivity of the material.

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Alistair McIlhagger is Director of the Advanced Future Materials and Manufacturing Group at Ulster University with approximately £14 million of funding. He held a Royal Academy of Engineering Industrial Fellowship and was lead in specialist training in aerospace for 7 years. He has published >75 papers with his research focusing on advanced preforming technologies including 3D weaving and associated technologies.

The objective of this review is to provide a comprehensive discussion of the existing literature on the development of high-performance, electrically conductive PEEK composites. Details on the characterization of these composites and a comparative assessment of the electrical, mechanical and rheological properties are presented. Finally, current and potential applications have been considered.

MECHANISM OF ELECTRICAL CONDUCTIVTY IN CONDUCTIVELY FILLLED POLYMERS

In conductively filled polymers, an electrically conductive filler is dispersed in a non-conductive polymer matrix. Two challenges of the way of formation of the conducting paths and the way of conduction after the formation of the paths relate to the mechanism of electrical conductivity in conductively filled polymers. The percolation, effective medium, microstructure and the thermodynamic theories are associated with the first challenge.[47–49] However, percolation theory has been mostly applied to estimate the formation way of the conducting paths. Based on this theory, in a mixture of dielectric and electrical components, at a fraction of the electrical component which is the electrical percolation threshold the conductivity of the mixture increases sharply from the conductivity of the dielectric component towards the conductivity of the electric component.[49–61]

The statistical percolation theory estimates the dependence of electrical conductivity (σ) on filler concentration beyond the electrical percolation threshold with a power law of the form

$$\sigma = \sigma_0(\phi - \phi_c)^t \quad (1)$$

σ_0 is the conductivity of the fillers, ϕ is the filler volume fraction, ϕ_c is the critical volume fraction at the electrical percolation threshold and t is the critical parameter that defines the dimensionality of the system. Usually, experimental results are fitted by plotting log σ *versus* log($\phi - \phi_c$) and incrementally varying ϕ_c until the best linear fit is obtained.[50,62–66]

Theories of contact conduction, the tunnelling effect, dielectric breakdown and field emission are associated with the second challenge. However, electron tunnelling is considered as the dominant mechanism around the percolation threshold. In general, an energy barrier exists in insulating materials such as polymers that prevents transfer of electrons from one electrode to another. In conductively filled polymers insulating layers form around the fillers which limit the physical contact between the particles and reduce the electrical conductivity. Electrons must break into the conduction band of the insulating layers to produce an electrical current. According to classical physics this is not possible since electrons cannot diffuse through the barrier unless the electron energy is equal to or more than the interfacial barrier. However, based on quantum mechanics, when the distance between neighbouring particles is sufficiently small and there is a driving force for movement of electrons, they can penetrate through the barrier by tunnelling. Therefore, electrons in conductively filled polymers form a particle/polymer pathway by tunnelling one by one from one particle electrode to the nearest particle electrode. Generally, the conductance of the composites is controlled by the conductivity of the insulating polymer and tunnelling effect when the distance between two particles is more and less than 10 nm respectively.[67–69] In the tunnelling contact model

Allaoui *et al.*[70] estimated the electrical conductivity of CNT filled polymers based on the tunnelling effect.[71–76]

ELECTRICALLY CONDUCTIVE PEEK COMPOSITES

Composite synthesis

Solution mixing and melt blending have been most commonly utilized to manufacture electrically conductive PEEK composites and nanocomposites.

PEEK/CNT composites

Díez-Pascual *et al.*[28,30] incorporated PEI, poly(bisphenol-A-ether sulfone) (PSF) and poly(1-4-phenylene ether-ether sulfone) (PEES) wrapped laser grown (LG) and purified arc grown (AP) single-wall CNTs (SWCNTs) (0.1, 0.5 and 1 wt%) into PEEK (150P). AP-SWCNTs were purified by a reflux of NH_3 to eliminate amorphous carbon particles and reduce metal catalyst content. Oxygenated groups were formed during the purification that increased the interaction of CNTs with compatibilizers and their adhesion to the polymer matrix. LG-SWCNTs were used without further purification since the content of residual catalyst was lower than 4%. In the wrapping process a solution of the compatibilizer with an organic solvent was mixed with the SWCNTs using stirring and subsequently an ultrasonic tip to improve the interaction of the CNT bundles and the compatibilizer. The mixture was filtered and dried under vacuum at 60 °C. SWCNTs and ground PEEK powder were then stirred and sonicated in ethanol, dried in an oven and blended in a micro-extruder at 380 °C. Thin films of the extrudate were prepared using a hot press. In two other studies, Díez-Pascual *et al.*[29] and Ashrafi *et al.*[12] applied the same PEEK/LG, AP and PEES wrapped SWCNT composite films to prepare electrically conductive PEEK/glass fibre (GF) laminates. The laminates were manufactured by putting down alternately four plies of glass fibre between five PEEK/SWCNT films. The materials were consolidated under a hot press with optimized pressure to reduce the porosity and enhance the fibre impregnation. Bangarusampath *et al.*[77] added catalytic carbon vapour deposition MWCNTs (2, 5, 10 and 17 wt%) to PEEK (Victrex 151) using a twin-screw extruder to manufacture nanocomposites. The nanocomposite containing 17 wt% of MWCNTs was then diluted to loadings of 0.25, 0.5, 1 and 1.5 wt% nanotubes in PEEK. The nanocomposite granules were hot compression moulded into disks for further characterizations. Mohiuddin and Hoa[24] added chemical vapour deposition (CVD) MWCNTs (1–15 wt%) to PEEK using melt blending to manufacture electrically conductive PEEK composites. Lin *et al.*[78] and Na *et al.*[18] incorporated processing aids of poly(aryl ether ketone) (FPEDEKKLCP) (0–5 wt%) and granular GENIOPLAST® Pellet S (GPPS) to PEEK /CVD MWCNT (7 wt%) composite using a twin-screw extruder to prepare electrically conductive composites.

PEEK/GNP composites

Yang *et al.*[31] incorporated 3-triethoxysilylpropyl-amine (KH550) functionalized graphene (CRG-KH550) (0.3–8 wt%) and thermally reduced graphene nanosheets modified by PES (m-TRG) (0.5–5 wt%) into PEEK using an ultrasonic bath to manufacture electrically conductive PEEK composites. Chen *et al.*[26] incorporated GNPs (0.1–10 wt%) into PEEK (151PF) using ultrasonic bath mixing (wet) and an electric powder mixer (dry) to prepare electrically conductive PEEK composite powders for laser sintering. Composite films were manufactured by controlled heating and cooling of the powders on glass sides on a hot plate. GNPs

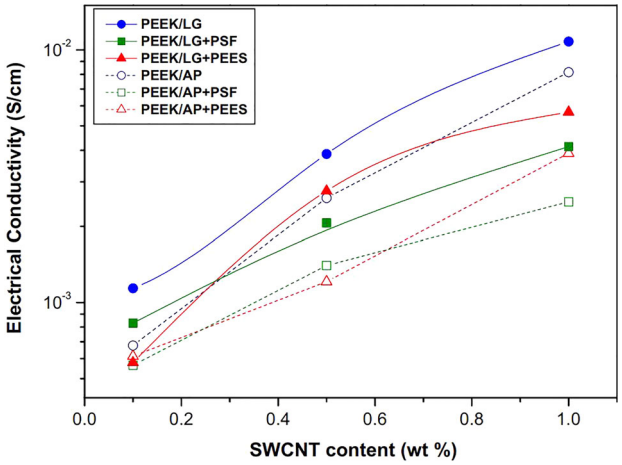

Figure 1. The room temperature DC volume conductivity of different PEEK/SWCNT nanocomposites. Adopted from reference 30 with permission. Copyright 2010, Elsevier.

(0–9 wt%) and carbonized loofah (CLF) (0–5.5 wt%) were loaded into PEEK using hot compression moulding to prepare electrically conductive PEEK composites by Li *et al.*[17] Pan *et al.*[16] manufactured electrically conductive PEEK composites through the inclusion of GNP flakes (3–6 wt%) into PEEK using ball milling, ultrasonic bath, cold and hot pressing.

Other PEEK composites

Rivière *et al.*[41,79] dispersed spherical AgNPs (diameter 100 nm, aspect ratio of 1) (9.5–59.5 wt%) and AgNWs (diameter 40 mm, thickness 180 nm) (4.1–40.4 wt%) in PEEK powder (2000PF) by stirring in ethanol and then drying in an evaporator. The dried powders were hot pressed to manufacture PEEK/Ag nanocomposites. Reilly and Kamel[43] mixed 10 vol% of Ni powder, with a mean particle size between 35 and 100 μm, with coarse and fine PEEK powders of medium molecular weight grades 150P and 150FP and high molecular weight grades 450P and 450FP to obtain a uniform coating of Ni particles on the surface of the PEEK particles. The powders were cold compacted to at least 60% relative green density by applying pressure up to 650 MPa to manufacture samples for volume electrical resistivity measurements. Goyal[44] dispersed EG (1–10 wt%) and PEEK (5300PF) in absolute ethanol using an ultrasonic bath for 30 min. The mixture was dried at 120 °C and PEEK/EG nanocomposite samples were prepared by a hot press technique at 380 °C. Extrand[80] compounded stainless steel fibre (SSF), carbon powder (CP) and carbon fibre (CF) with PEEK and injection moulded samples for characterization.

Electrical properties

Direct current (DC) electrical conductivity

PEEK/CNT composites. Díez-Pascual *et al.*[30] reported a sharp increase in room temperature volume electrical conductivity of PEEK from 10^{-13} S cm^{-1} to about 10^{-3} S cm^{-1} with the addition 0.1 wt% of SWCNTs. Also, as shown in Fig. 1, the electrical conductivity of the composites did not increase significantly with an increase of SWCNT loading up to 1 wt% indicating that an SWCNT content of 0.1 wt% was beyond the electrical percolation threshold. PEI wrapped SWCNTs decreased the electrical conductivity of the nanocomposites by one order of magnitude. However, nanocomposites containing PSF and PEES wrapped SWCNTs indicated almost the same level of electrical conductivity as non-

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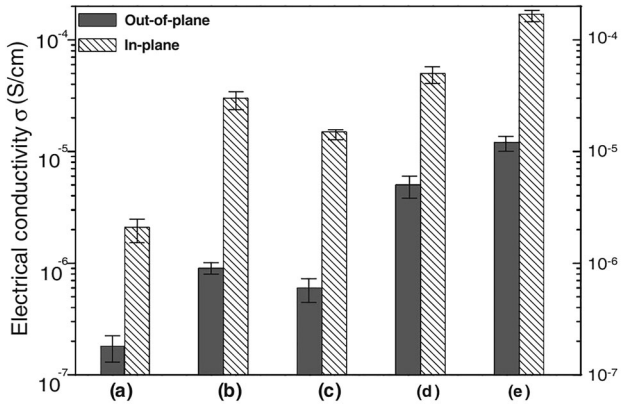

Figure 2. The in-plane and out-of-plane room temperature DC volume conductivities of PEEK/GF laminates: (a) PEEK/AP(1 wt%)/GF, (b) PEEK/LG (1 wt%)/GF, (c) PEEK/LG(0.5 wt%) + PEES/GF, (d) PEEK/AP(1 wt%) + PEES/GF, (e) PEEK/LG(1.0 wt%) + PEES/GF. Reprinted from reference 29 with permission. Copyright 2011, Elsevier.

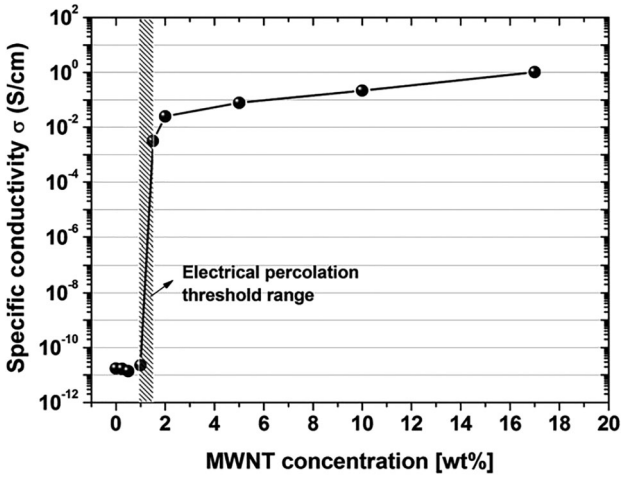

Figure 3. The specific conductivity of the composites at a fixed frequency of 1 Hz. Reprinted from reference 77 with permission. Copyright 2009, Elsevier.

compatibilized nanocomposites. At the low SWCNT loading of 0.1 wt%, the type of SWCNTs did not affect the electrical conductivity of the nanocomposites, although the nanocomposites containing LG-SWCNT without further treatment exhibited higher conductivity than nanocomposites loaded with purified AP-SWCNT at higher loadings.[81–88]

In another study, Díez-Pascual *et al.*[29] showed (Fig. 2) that PEEK/SWCNT composites increased the electrical conductivity of GF laminates to more than 10^{-8} S cm^{-1} which is required to avert the accumulation of static charge. The electrical conductivity of the PEEK/SWCNT/GF laminates was affected by the direction of the measurement, the degree of fibre impregnation and the type and concentration of the SWCNTs. The in-plane conductivity of the laminates was in the range of 10^{-6}–10^{-4} S cm^{-1} which was about one order of magnitude higher than the through-plane conductivity. This was ascribed to the in-plane reinforcement of fibre that prevented the development of the conductive paths through the thickness. Increasing the SWCNT loading from 0.5 to 1 wt% raised the electrical conductivity of the laminates by about one order of magnitude. Also, laminates including LG-SWCNTs had higher electrical conductivity than AP-SWCNTs, and wrapped SWCNTs increased the electrical conductivity of the laminates by about one order of magnitude above that for non-compatibilized SWCNTs.[12,30]

Bangarusampath *et al.*[77] showed (Fig. 3) that a CNT content of between 1 and 1.5 wt% was sufficient for electrical percolation since the electrical conductivity of PEEK increased abruptly by at least nine orders of magnitude to about 10^{-3} S cm^{-1}. At the electrical percolation threshold, CNTs had sufficient proximity to allow electron hopping or tunnelling.

Mohiuddin and Hoa[24] reported that the electrical conductivity of PEEK/MWCNT composites increased sharply between 3 and 4 wt% loading of MWCNTs indicating that the electrical percolation threshold had been attained. Samples were then prepared at loadings between 3 and 4 wt% of MWCNTs in order to more precisely identify the threshold. It was noted that the electrical conductivity increased abruptly between 3.5 and 3.6 wt% to 2.26×10^{-10} S cm^{-1} from a value of 5.18×10^{-15} S cm^{-1} for pure PEEK. Also, the electrical conductivity reduced at 15 wt%

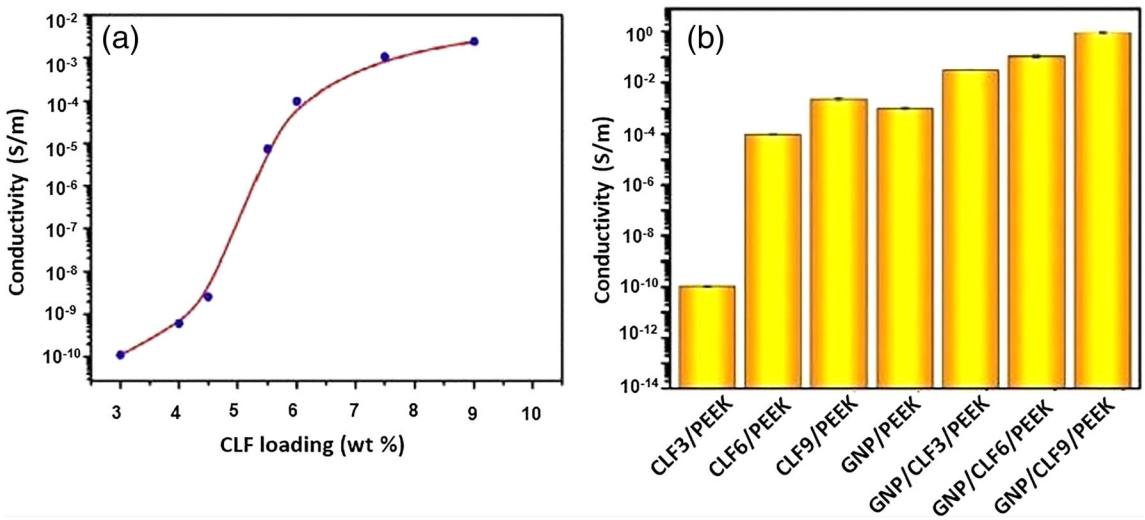

Figure 4. (a) Dependence of DC electrical conductivity of PEEK/CLF composites on CLF content. (b) DC electrical conductivity as a function of CLF loading for PEEK/CLF and PEEK/GNP/CLF composites (containing 2.5 wt% of GNP in all PEEK/GNP/CLF composites). Adopted from reference 17 with permission. Copyright 2019, Elsevier.

compared with 10 wt% due to the formation of MWCNT agglomerates which led to a reduction in the conductive paths. In addition, upon increasing the temperature from 20 to 140 °C, the electrical conductivity of the composite containing 8 wt% MWCNTs increased in a concave downward manner while that of the composite with 10 wt% MWCNTs increased in a concave upward manner. Increasing temperature in both cases increases electronic movement and thus conductivity. However, in the 8 wt% MWCNT composites, tunnelling is the primary mode for conductivity and as temperature increases the gap between MWCNTS also increases thus leading to a concave downward trend as temperature increases further. The 10 wt% MWCNT composites have good particle–particle contacts and do not depend on tunnelling for conductivity. They increase in conductivity in a concave upward manner as reduced matrix modulus at higher temperatures enables even more contacts to be formed. The change in electrical conductivity with repeated thermal cycles was also investigated for a potential thermistor application. The electrical conductivity increased during the heating cycle due to electron emission at higher temperatures and it increased slightly more during the cooling cycle because of re-agglomeration of MWCNTs. Also, in another study Mohiuddin and Van Hoa[89] reported the effect of pressure on the electrical conductivity of the composites containing 8, 9 and 10 wt% of MWCNTs at temperatures of 20 and 140 °C and found that the electrical conductivity increased with increasing pressure at both temperatures due to an increase in the tunnelling effect and the contacts between tubes. The effect of pressure was more pronounced at room temperature, but it is not clear why this occurred.

PEEK/GNP composites. Chen *et al.* [26] reported that PEEK with 0.1–10 wt% of GNP produced by the wet and dry methods changed the electrical conductivity from 7.14×10^{-12} to 4.54×10^{-3} S cm^{-1} and from 4×10^{-12} to 4.35×10^{-3} S cm^{-1} respectively and their electrical percolation thresholds occurred between 1 and 5 wt%. It was shown by Li *et al.*[17] (Fig. 4) that the DC electrical conductivity of the individual CLF was about 2.4 S cm^{-1} and that the incorporation of 3–9 wt% CLF to PEEK raised its electrical conductivity to 2×10^{-7} from

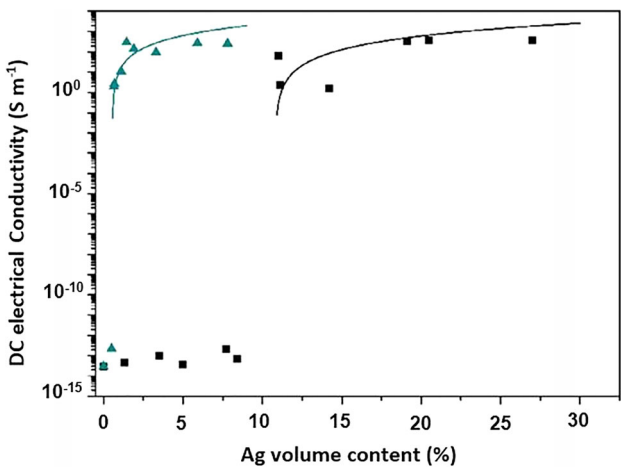

Figure 5. Room temperature DC electrical conductivity of PEEK/Ag nanocomposites at different Ag concentrations at room temperature: black symbols, PEEK/AgNP nanocomposites; blue symbols, PEEK/AgNW nanocomposites; –, power law fit. Adopted from reference 41 with permission. Copyright 2016, Elsevier.

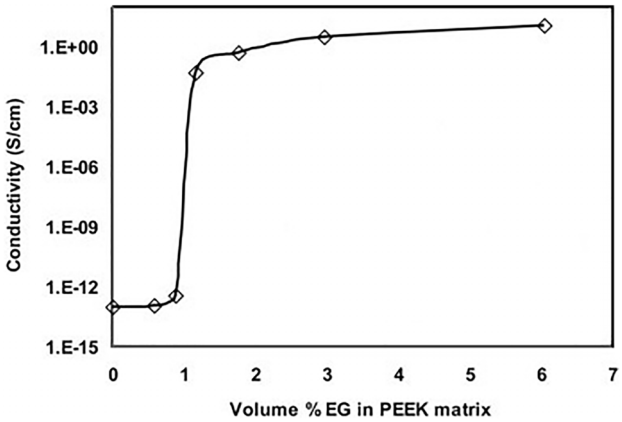

Figure 6. DC electrical conductivity of the PEEK/EG nanocomposites. Adapted from reference 44 with permission. Copyright 2013, Elsevier.

1.1×10^{-13} S cm^{-1} with the electrical percolation threshold of the PEEK/CLF composites occurring at 4.09 wt%. The addition of GNP/CLF (9 wt%) to PEEK resulted in an electrical conductivity of 9.4×10^{-3} S cm^{-1} due to physical contact between the fillers.

The electrical percolation threshold of PEEK/GNP composites manufactured by Pan *et al.*[16] occurred at 3 wt% with an electrical conductivity of 10^{-5} S cm^{-1}.

Other PEEK composites. As shown in Fig. 5 the electrical percolation thresholds of PEEK/AgNP and PEEK/AgNW, based on the power law, occurred at Ag concentrations of 49 wt% (10.8 vol%) and 4.1 wt% (0.55 vol%) respectively.[41] The huge difference between the electrical percolation thresholds of the two nanocomposites was attributed to the high aspect ratio of AgNW which facilitated the formation of conductive paths at low concentration levels.[41,79]

Reilly and Kamel[43] applied pressure to mixtures of PEEK/Ni powders to localize high plastic deformation of the metal particles at the interfaces between PEEK particles which led to mechanical interlocking and formation of conductive paths during the compaction process. Resistivity values for Ni-filled 150P, 150PF, 450P and 450PF composites were 0.06, 1.38, 0.08 and 0.76 Ω cm, corresponding to high electrical conductivities of 16.67, 0.72, 12.5 and 1.32 S cm^{-1} respectively. Also, it was reported in this study that the electrical resistivities of the Ni-filled 450P and 150P materials were an order of magnitude lower than comparable injection moulded materials. This is likely to be due to better nanoparticle dispersion and more particle–particle contact in injection moulded material compared with solid compaction.

Goyal[44] showed (Fig. 6) that electrical conductivity sharply increased between EG loadings of 1.5 wt% (0.87 vol%) and 2 wt % (1.16 vol%) suggesting that the electrical percolation threshold was at 1.5 wt%. Also, the electrical percolation threshold estimated using the power law was almost the same at 0.8 vol%. Very high electrical conductivities of 0.05, 3.24 and 12.3 S cm^{-1} were obtained at EG contents of 2, 5 and 10 wt%.

Extrand[80] indicated that the incorporation of CP, CF and SSF into PEEK increased its surface resistivity to $>10^{4.9}$, $10^{6.1}$ and $10^{8.3}$ Ω square^{-1} from $10^{14.3}$ Ω square^{-1} which resulted in static dissipative PEEK/CF and PEEK/SSF composites and conductive PEEK/CP composites. Neat PEEK had a long decay time whilst all the composites dissipated both negative and positive charges immediately.

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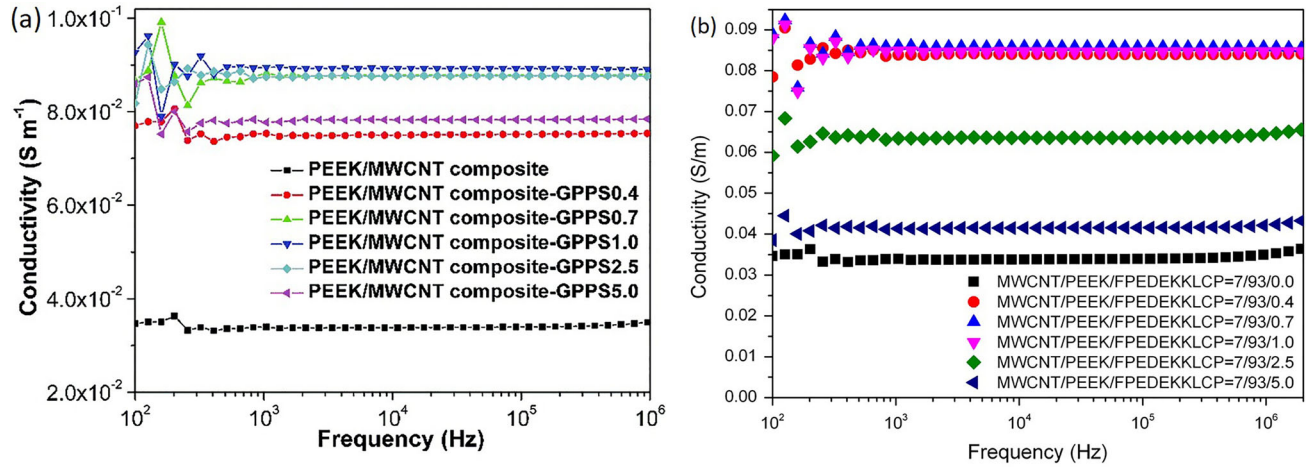

Figure 7. (a) The effect of GPPS concentration (reprinted from reference 18 with permission; Creative commons 2018, Royal Society of Chemistry) and (b) the effect of FPEDEKKLCP concentration (reprinted from reference 78 with permission; Copyright 2017, SAGE Publications) on the AC conductivity of PEEK/MWCNT composites at room temperature.

Alternating current (AC) electrical conductivity

PEEK/CNT composites. Lin *et al.*[78] and Na *et al.*[18] demonstrated (Fig. 7) that the AC electrical conductivity of the PEEK/MWCNT composites at room temperature increased by about 140% and 154% from 3.50×10^{-4} to 8.4×10^{-4} and 8.9×10^{-4} S cm^{-1} with a loading of 0.4 wt% of FPEDEKKLCP and 1 wt% of GPPS respectively due to improved dispersion of MWCNTs in the matrix. Also, the AC electrical conductivity of the PEEK/MWCNTs decreased to 6.44×10^{-4} and 4.21×10^{-4} S cm^{-1} and 8.8×10^{-4} and 7.8×10^{-4} S cm^{-1} by incorporation of 2.5 and 5 wt% of FPEDEKKLCP and GPPS respectively because of the reduction in the content of MWCNTs in the matrix.

PEEK/GNPs composites. Yang *et al.*[31] reported the AC electrical conductivity behaviour of PEEK/CRG-KH550 and PEEK/m-TRG composites at a frequency of 10^3 Hz that is well described by the power law, with electrical percolation thresholds of the composites at 0.3 wt% (0.2 vol%) and 1 wt% (0.76 vol%) respectively.

Mechanical properties

PEEK/CNT composites

Díez-Pascual *et al.*[28,30] showed via dynamic mechanical analysis (DMA) that the incorporation of 1 wt% of PEI and PSF wrapped LG-SWCNTs improved the storage modulus of the nanocomposites at room temperature by about 36% and 35% and raised the glass transition temperature (T_g) of PEEK by 9 and 15 °C respectively. The SEM results showed that PEI induced disaggregation and disentanglement of SWCNTs and reduced the filler domains in the matrix which led to improved interfacial adhesion and more efficient stress transfer between SWCNTs and PEEK. Polysulfones had a dual affinity with PEEK and the SWCNTs due to interaction of their phenyl groups with the matrix and the hexagonal networks of the nanofillers. Additionally, the compatibilization effect enhanced by chemical interaction of the polar segments of polysulfones to surface groups of the SWCNTs improved nanofiller dispersion and CNT–polymer load transfer. Therefore, the mechanical properties of these composites are higher than those reinforced by pristine CNTs.

Díez-Pascual *et al.* [29] and Ashrafi *et al.*[12] investigated the mechanical properties of the laminates using DMA tests. The addition of 1 wt% of AP and LG-SWCNTs only enhanced the storage modulus of PEEK/GF at temperatures below the glass transition of PEEK by 5% and 8% respectively whereas inclusion of the same amount of PEES wrapped AP and LG-SWCNTs improved the storage modulus by about 18% and 21% respectively. This was attributed to better dispersion and improved interfacial adhesion of wrapped SWCNTs in the matrix which caused more uniform load distribution, more efficient shear transfer and better fibre impregnation. However, the modulus increment of PEEK/GF was more pronounced at higher temperatures due to a reduction of PEEK modulus relative to the SWCNT modulus at increasing test temperature; 1 wt% wrapped AP-SWCNTs increased the storage modulus of PEEK/GF by 75% at a temperature of 200 °C. In addition, 1 wt% of PEES wrapped AP and LG-SWCNTs raised the T_g of the PEEK/GF by an average of 18% and 21% respectively while the same amount of unwrapped AP and LG-SWCNTs increased the T_g by 5% and 8% respectively. Moreover, tan δ reduced with the incorporation of SWCNTs into PEEK/GF laminates due to a reduction in chain mobility caused by the presence SWCNTs with a reduction of 35% for the 1 wt% wrapped LG-SWCNTs.

Lin *et al.*[78] and Na *et al.*[18] showed that the incorporation of FPEDEKKLCP and GPPS decreased the shear viscosity of the PEEK/MWCNTs which led to better dispersion of the MWCNTs in the matrix. The elongation at break of PEEK/MWCNTs increased from 37% to 47% and 46.4% by inclusion of 0.4 wt% of FPEDEKKLCP and 0.7 wt% of GPPS respectively due to a reduction of particle agglomeration and thus stress concentration. Incorporation of FPEDEKKLCP and 0.4–1 wt% of GPPS did not change the tensile strength of the PEEK/MWCNTs.

PEEK/GNP composites

Yang *et al.*[31] reported that the inclusion of m-TRG produced little change in the tensile strength of PEEK, increased its Young modulus from 2.2 to 3.07 GPa at 3 wt% and decreased its elongation at break drastically. In addition, the incorporation of 0.1, 0.5 and 1 wt % of GNPs into PEEK by the wet and dry methods raised the stress at maximum load by 17%, 23% and12% and 25%, 21% and 9% respectively compared with the pure PEEK while incorporation of 5 wt% GNPs decreased the stress at the maximum load by 48%. Also, the strain at maximum load of the composites containing 0.5 and 1 wt% increased by 33% compared with the pure PEEK.[26]

Table 1. Composition, preparation method and different properties of electrically conductive PEEK composites at room temperature

Sample no.	Composition (wt%)	Processing method	Electrical percolation threshold (S cm^{-1} at wt%)	Maximum electrical conductivity (S cm^{-1} at wt%)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)	T_g (°C)	Storage modulus (GPa)	Ref. no.
PEEK/CNTs										
1	PEEK/LG-SWCNT (0.1–1)	U+MB+HCM	10^{-3} at 0.1	10^{-2} at 1	130–139	11.4–6.4	4.6–5.1	. 152.2-154	4.7–4.9	30
2	PEEK/CLG-SWCNT (0.1–1)	U+MB+HCM	1×10^{-4}–8×10^{-4} at 0.1	3×10^{-4}–3×10^{-3} at 1	132–147	11.9–8.9	4.6–5.7	153.5–163.3	4.5–5.3	28, 30
3	PEEK/AP-SWCNT (0.1–1)	U+MB+HCM	7×10^{-4} at 0.1	8×10^{-3} at 1	128–138	11.2–6.6	4.5–4.9	151.1–155.3	4.2–4.6	30
4	PEEK/CAP-SWCNT (0.1–1)	U+MB+HCM	8×10^{-5}–5.5×10^{-4} at 0.1	2×10^{-4}–2×10^{-3} at 1	128–144	13.2–9.7	4.5–5.5	154.3–164.1	4.4–5.5	28, 30
5	PEEK/MWCNT (2–17)	MB+HCM	3×10^{-3} at 1.5	1 at 17	–	–	4.6–6	–	–	77
6	PEEK/MWCNT (1–15)	MB+HCM	2.3×10^{-10} at 3.6	10^{-5} at 10	–	–	–	–	–	24
PEEK/GNPs										
7	PEEK/RG-KH550 (0.3–8)	U+HCM	8×10^{-12} at 0.3	10^{-4} at 8				–	–	31
8	PEEK/m-TRG (0.5–5)	U+HCM	4×10^{-10} at 1	2×10^{-3} at 5	96-106	4.7-35	2.4-3.1	–	–	31
9	PEEK/CLF (3–9)	HCM	6×10^{-12} at 4.09	2×10^{-5} at 9	–	–	–	–	–	17
10	PEEK/GNP (2.5)/CLF (3–9)	HCM	–	9.4×10^{-3} at 9	–	–	–	–	–	17
11	PEEK/GNP (3–6)	SM+HCM	10^{-5} at 3	10^{-3}at 6	–	–	–	–	–	16
12	PEEK/GNP (0.1–10)	U	7.7×10^{-4} at 5	4.5×10^{-3} at 10	42.5–100	1.7-5.9	–	–	–	26
13	PEEK/GNP (0.1–10)	EPM	10^{-4} at 5	4.3×10^{-3} at 10	52–102	1.8-6.5	–	–	–	26
Other conductive PEEK composites										
14	PEEK/AgNP (9.5–59.5)	SM+HCM	0.02 at 49	2 at 59.5	–	–	–	–	–	41, 79
15	PEEK/AgNW (4.1–40.4)	SM+HCM	0.02 at 4.1	2 at 40.4	–	–	–	–	–	41
16	PEEK/EG (1–10)	U+HCM	0.1 at 1.5	12.3 at 10	–	–	–	–	–	44
17	PEEK/Ni -41.4	CCM	–	16.67 at 41.4	–	–	–	–	–	43

AgNP, silver nanoparticle; AgNW, silver nanowire; CAP-SWCNT, compatibilized purified arc grown single-wall carbon nanotube; CCM, cold compression moulding; CLF, carbonized loofah; CLG-SWCNT, compatibilized laser grown single-wall carbon nanotube; EG, expanded graphite; EPM, electric powder mixer; GNP, graphene nanoplatelet; HCM, hot compression moulding; LG-SWCNT, laser grown single-wall carbon nanotube; MB, melt blending; m-TRG, thermally reduced graphene nanosheets modified by poly(ether sulfone); MWCNT, multi-wall carbon nanotube; RG-KH550, 3-triethoxysilylpropyl-amine functionalized graphene; SM, solution mixing; U, ultrasonication.

Li *et al.*[17] showed that the addition of 2.5 wt% of GNPs to the PEEK matrix decreased its compressive strength from 140 to 64.2 MPa due to the weak interface created by GNP stacking whilst the incorporation of 3 wt% of CLF raised the compressive strength of the PEEK/GNP (2.5 wt%) to 114.6 MPa because of better interfacial interaction between CLF and the matrix. However, the addition of more CLF to the PEEK/GNP composites reduced the compressive strength due to defects inside the composites generated by the CLF. The compressive modulus of the composites increased as the filler content increased.

Comparison and discussion

A summary of the research on electrically conductive PEEK composites is presented in Table 1.

The electrical percolation threshold (ϕ_c) describes the interconnectivity of the fillers which is dependent on the matrix properties such as viscosity and surface tension, filler properties such as orientation, geometry, concentration, distribution and surface chemistry and the composite manufacturing method. Viscosity and surface tension of the matrix affect ϕ_c by contributing to the dispersion and distribution of the fillers. However, PEEK materials with similar viscosities and surface tensions were utilized in the composites in Table 1; hence the matrix properties should have a negligible effect on the electrical percolation threshold of the composites. Based on the concept of excluded volume, ϕ_c is inversely proportional to the filler aspect ratio or shape anisotropy. Also, the processing method and processing aids influence ϕ_c by affecting the orientation, dispersion, distribution and aspect ratio of the fillers in the PEEK matrix. Generally, a higher aspect ratio and better dispersion and distribution of the conductive fillers in the matrix lead to a lower electrical percolation threshold and higher conductivity. This is due to (i) a decrease in the gap between fillers which increases the tunnelling effect and (ii) an increase in contacts or conductive paths created between fillers that enhance the flow of electrons in the composites.

A comparison of the electrical properties of composites 1 to 4 indicates that the incorporation of the wrapped SWCNTs into the PEEK matrix slightly decreased the value of the electrical conductivity due to a reduction in the number of contacts and an increase in the gap between tubes compared with non-compatibilized SWCNTs. Also, composite 1 exhibited higher conductivity than composite 3 due to more defects, lower quality and the smaller aspect ratio of AP-SWCNTs.[28,30,81–88]

Composite 6 has a much bigger ϕ_c and lower conductivity than composite 5 which could be ascribed to the fact that MWCNTs of composite 6 were in an entangled state due to use of a melt blending method that did not provide sufficient shear rate to disperse MWCNTs adequately in the matrix.[24] Composite 5, however, was obtained by a further dilution of a master batch containing 17 wt% MWCNTs that applied additional shearing in the manufacturing stage resulting in more uniform distribution of tubes, more contacts and smaller gaps between them.[24,77]

PEEK/SWCNT composites exhibited higher conductivity and smaller electrical percolation thresholds than PEEK/MWCNT composites. This can be attributed to the fact that the pristine MWCNTs obtained by CVD had a higher density of defects and a lower aspect ratio compared with LG and AP-SWCNTs due to the lower temperature applied during the CNT manufacturing. Also, ultrasound and wrapping were used to disperse the SWCNTs in the PEEK matrix leading to higher aspect ratio, looser entanglements and better debundling and distribution of SWCNTs in the PEEK matrix compared with melt blending.[28,30]

Composites 7 and 8 exhibited a very low electrical percolation threshold compared with other PEEK/GNP composites due to better dispersion of GNPs in the matrix. This was achieved by a combination of ultrasonic processing and compatibilization of GNP by KH550 and PES. However, composite 12 which was also obtained by using ultrasonic processing exhibited a value of ϕ_c that was bigger than that of composites 7 and 8 and in the same range as composites 11 and 13 which were manufactured without ultrasonication. This can be ascribed to the lack of a hot compression moulding stage in the processing of composite 12 that could orient GNP platelets in the pressure direction and increase contacts and reduce the gap between them.

CNTs enhanced the electrical conductivity of PEEK more than GNPs. This behaviour can be attributed to the fact that rod-like and more flexible one-dimensional CNTs have extremely large lengths (microscale) compared with their diameters (nanoscale) that helps them to form a percolation network more effectively at lower fractions than more rigid two-dimensional GNP platelets.[90,91] Also, the size and geometry of GNPs allow significant plane-to-plane contact that makes them aggregate more readily than CNTs. Moreover, it is also possible that the contact resistance between CNT particles is lower than that between GNPs.[92]

Composite 16 containing EG as a carbon filler has a very high electrical conductivity at a low electrical percolation threshold compared with composites made with CNTs and GNPs. This may be ascribed to a better mixing procedure and the higher aspect ratio of EG which formed a three-dimensional network in the PEEK matrix. Additionally, PEEK chains diffuse into the pores of the honeycomb-like structure of EG during processing forming a conductive, interconnected network.[44,93]

Composites 14 and 17 containing microscale spherical metal particles with an aspect ratio of 1 exhibited much higher ϕ_c and higher conductivity due to much lower surface area and higher conductivity of the metal particles compared with the other conductive nanofillers.

Also, it is clear from Table 1 that PEEK/CNT composites exhibit higher mechanical properties than PEEK/GNP composites. The mechanical properties of both fillers are similar since they are carbon-based nanomaterials but the combination of compatibilizer and ultrasonication in the preparation of the PEEK/CNT composites led to better dispersion and filler–matrix interaction and thus more effective load transfer between CNTs and PEEK.[91]

Applications

The electrical conductivity required to prevent the buildup of static charges in materials is 10^{-8} S cm^{-1} while EMI shielding applications need a conductivity of 10^{-4} S cm^{-1}.[29,47,94] Based on Table 1, all PEEK composites apart from composites 6–13 provide the necessary electrical conductivity, at their electrical percolation thresholds, for the aforementioned applications. PEEK/GNP composites also exhibit the necessary conductivity but at higher filler loading. PEEK/MWCNT composites have been targeted at demanding applications in aerospace and defence with highly efficient EMI shielding and potential applications as thermistors.[18,24,27,94] Also, GNPs have been incorporated into PEEK/CLF and PEEK/CF composites to develop a high-performance EMI shielding material for extremely harsh environments such as warships and an electro-thermal de-icing material for communication antennas.[16,17] Also, future applications of electrically conductive PEEK composites may be extended by employing novel

manufacturing methods such as fused filament fabrication for applications in, for example, electronics and space, orthopaedics, oil and gas.[95–99]

CONCLUSIONS

This review delivers an overview of the research in PEEK composites filled with CNTs, GNPs and other inorganic and organic conductive fillers. These composites were designed for high-performance EMI shielding and electrostatic discharge materials for advanced technological applications. The main challenge in the manufacture of these composites is to achieve a balance of high conductivity enhancement without mechanical property deterioration and without detrimentally affecting processability. Good dispersion of fillers in the matrix is one of the key challenges to be overcome and can be obtained by applying various strategies including ultrasonication and modification of the filler surface chemistry by compatibilization. Among the fillers investigated, the incorporation of compatibilized, wrapped CNTs into PEEK using combined ultrasonication and melt blending reduced the electrical percolation threshold to the lowest concentration of CNTs and enhanced the mechanical properties more effectively than pristine CNTs due to better dispersion and improved interfacial adhesion. Also, various high temperature processing aids were incorporated into PEEK/CNT composites to reduce viscosity and improve the dispersion quality of CNTs in the matrix. Although they have excellent performance CNT filled composites are not particularly cost efficient since CNTs are generally more expensive than other conductive fillers. GNPs have also been successfully incorporated into PEEK to produce electrically conductive composites. Other studies have shown that EG, Ni, Ag, stainless steel, CP and CF have also been successful to various degrees in enhancing the electrical conductivity of PEEK but further research is required to optimize the performance of these composites.

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