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Effect of manufacturing processes on percolation threshold and electrical conductivity of polymer/multi layers graphene nanocomposites

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ABSTRACT

Electrical conductivities of the high performance poly(ether ketone)/multi layers graphene or graphite nanoplatelet (2-10 nm thick) (PEK/GNP) nanocomposites manufactured by three different methods were compared and studied. The percolation threshold of the nanocomposites manufactured by; planetary ball mill followed by hot pressing (method-1) and planetary ball mill followed by cold pressing + sintering (method-2) is lowest, i.e., 0.755 vol% (or 0.0076 volume fraction) GNP, while that of manufactured by a solution method followed by hot pressing (method-3) is about 1.21 vol%.The lower percolation threshold for the method-1 and method-2 was attributed to the better dispersion of GNP in the PEK matrix while the higher percolation threshold for the method-3 was attributed to a non-uniform dispersion of GNP and GNP-aggregates in the matrix. However, above percolation for a given volume fraction (i.e., 1.52 vol%), the electrical conductivities of the nanocomposites manufactured by method-3 showed higher values compared to those of method-1 and method-2. The electrical conductivity of the 3 vol% nanocomposite increased by >12 orders of magnitude as compared to pure matrix. The highest electrical conductivity of the nanocomposites manufactured by method-3 is 1004 S/cm which is interesting.

1. Introduction

Polymer matrix nanocomposites filled with nano-sized conductive fillers have been widely studied since the discovery of carbon nanotubes (CNTs) in 1991. Many carbon based materials such as carbon fibers, carbon nanofibers (CNFs), CNTs, expanded graphite, few layer graphene, and graphene [1–3] have been used as conductive fillers to fabricate composite materials for electromagnetic interference (EMI) shielding application because of their high electrical conductivity, excellent mechanical properties, and high specific stiffness [4]. However, in these polymer composites, individual fillers are randomly distributed inside the polymer matrix and are surrounded by the polymer chains. Thus, the electrical conductivity of the composites or nanocomposites strongly depends on electron percolation between the nearest filler particles. This has been achieved by the addition of a suitable (ranging from <0.01 to 0.50) volume fraction of the fillers depending upon the size and aspect ratio of fillers, and the degree of dispersion of the fillers in the polymer matrix. In general, fillers with a very high aspect ratio and good dispersion in the matrices are required to form an interconnected (or 3-dimensional) conductive network in the insulating matrix to improve the electrical conductivity and EMI shielding effectiveness (EMI SE) of the composites. The EMI SE of a composite mainly depends on the intrinsic conductivity, dielectric constant and aspect ratio of the fillers [5]. For a given filler loading, multi-walled carbon nanotube-filled polystyrene composites exhibited higher EMI shielding effectiveness compared to those filled with carbon nanofibers [6]. The EMI shielding of single-walled carbon nanotube (SWNT) filled epoxy nanocomposites were found to increase with increasing of aspect ratio and decrease in the wall defects of SWNTs [7]. Specifically, the electrical conductivity of ~0.01 S/cm is said to be the lowest value to obtain the EMI SE of 20 dB [8]. Polymer nanocomposites can be fabricated with excellent electrical properties without compromising mechanical properties [9]. Recently, it has been found that multilayer graphene or graphite nanoplatelet (GNP), due to extremely high aspect ratio and high electrical conductivity can provide excellent EMI-SE [9–12]. Moreover, the addition of graphene into the polymer matrix increases the thermal conductivity [13], dimensional stability [14], and tensile strength and modulus [15].

Poly(ether ketone) (PEK) is a high performance polymer exhibiting glass transition temperature (T_g) of 152 °C and melting temperature (T_m) of 370 °C. It also has a very high thermo-oxidative stability, excellent radiation resistance and good strength and modulus [16]. Due to its excellent unique combination of thermal and mechanical properties at room temperature as well as high temperature, PEK based

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composites/nanocomposites have gained importance for various applications. Therefore, the effect of the addition of CNTs [17] and CNFs [18] on its nanocomposites fabricated by melt mixing has been studied recently. However, despite a low cost of GNP compared to CNTs or graphene, the effect of GNP addition on electrical properties of the PEK/GNP nanocomposites were hardly studied so far. In view of this, current study reports for the first time the comparison of electrical conductivities for the PEK/GNP nanocomposites manufactured by three methods; planetary ball mill followed by hot pressing (method-1), planetary ball mill followed by cold pressing + sintering (method-2) and solution method followed by hot pressing (method-3). The distribution of GNP in the matrix was examined by field emission scanning electron microscopy (SEM).

2. Experimental work

2.1. Materials

Commercial poly(ether ketone) (PEK) (1100 PF grade) powder donated by Gharda Chemicals Ltd., Thane (Mumbai), India, was used as matrix. Graphene powder (purity 99.99%) with thickness 2–10 nm purchased from D&D Advanced Materials, Pune, India was used in as received condition. The Raman spectroscopy of this powder was carried out to confirm whether it is graphene or multilayered graphene sheet. It is well known that the position of G-band is highly sensitive to the number of graphene monolayers present in the sample. It can be clearly seen from the Fig. 1 that the position of G-band is at 1583.73 cm^{-1} which is lower than 1587.94 cm^{-1} (for single-layer) and 1584.16 cm^{-1} (for two-layer graphene). However, this value is higher than that of 1581.72 cm^{-1} (for pure graphite) indicating that the graphene powder has more than two layers in the individual sheets. A broad 2D peak indicates overlapping of individual modes of multiple graphene layers. Furthermore, $I_{2D}/I_G = 0.7197$ indicating that the filler powder is multilayered graphene or Graphite Nanoplatelets (GNPs). Hence, this filler powder is reported as GNPs in this study.

2.2. Manufacturing of PEK/GNP nanocomposites

The PEK and appropriate weight of GNP powders were milled (or blended) using a planetary ball mill (Retsch Technology, Germany, PM 200) for a total milling time of 5 h at 250 rpm with balls to powder ratio (BPR) of 10:1 in dry state. The milled powders were hot pressed using a 15 T hot compaction machine (Kimaya Engineering, India) under a pressure of 60 MPa at a temperature of 390 °C. After the dwell time of 20 min, the samples were cooled naturally to about 100 °C and then the samples were ejected. This method was called hot pressing and named as method-1. In second method (called as method-2), the milled PEK/GNP powders obtained after planetary ball mill were compacted at room temperature (called cold pressing) under 350 MPa pressure and dwell time of 10 min. The prepared green pellets were sintered at 260 °C for a sintering time of 10 h in a vacuum oven. After sintering, the samples were cooled naturally to a room temperature. In third method (method-3), the required weight of GNP powder was added to dimethylformamide (DMF) and ultrasonicated for 30 min and then an appropriate quantity of PEK powder was added into GNP/DMF suspension. The PEK/GNP/DMF slurry was then subjected to concurrent magnetic stirring and heating till a dry powder was obtained. Then, the PEK/GNP powder was dried in a vacuum oven. Finally, the dried powders were hot pressed using the method as mentioned above and this method was named as solution suspension (SS) method followed by hot pressing, i.e., method-3. A brief summary of methods used in this work is given in Table 1. The GNP content was varied from 0 to 5 wt% with a corresponding 0 to 3.06 vol% which were calculated using the equation: $V_f = W_f / [W_f + W_m(\rho_f / \rho_m)]$, where, W_f is the weight fraction, and ρ_f is the density of GNP (density: 2 g/cm^3). The volume fraction of GNPs can be calculated by dividing vol% by 100. W_m and ρ_m are the weight fraction and density of the PEK matrix, respectively. The density of PEK was considered as 1.30 g/cm^3.

Table 1
List of methods used for manufacturing PEK/GNP nanocomposites.

Code of manufacturing processes	Blending of PEK and GNP powders by	Final processing route
Method-1	Planetary ball mill (BM)	Hot pressing (HP)
Method-2	Planetary ball mill (BM)	Cold pressing (CP) + sintering
Method-3	Solution suspension (SS) method	Hot pressing

2.3. Characterization

Field Emission Scanning Electron Microscope (FE-SEM, Zeiss, Sigma HV) was used to investigate the morphology of pure GNP powder and fractured nanocomposite sample. The fractured surface of nanocomposites was coated with a thin layer of gold-palladium alloy using sputter coater to minimize charging effects. For the measurement of electrical conductivity, samples were coated with a thin coating of silver paste to avoid contact resistance. The resistance of samples above 1 MΩ was measured using Electrometer (Keithley 6517B). The resistance below 1 MΩ was measured using 7 1/2 digit multimeter (Keithley 2001). Then, the volume resistivity (ρ) was calculated by the relation $\rho = R.(A / L)$, where R is resistance, L is sample thickness and A is cross-sectional area of the sample. Electrical conductivity was reported as the reciprocal of volume resistivity.

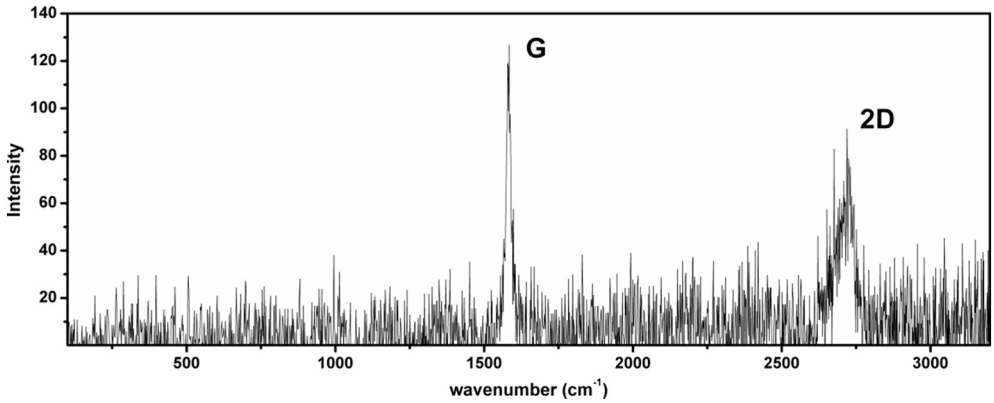

Fig. 1. Raman spectroscopy of GNP powder.