Supporting Information

Details of the characterization techniques; tables collecting DSC, TGA and DMA data of the nanocomposites investigated.

Scanning electron microscopy

The morphology and state of carbon nanotube dispersion within the PEEK matrix were evaluated with a Philips XL30 scanning electron microscope (SEM) applying an acceleration voltage of 25 kV and an intensity of $9 \cdot 10^{-9}$ A. The composite samples were cryo-fractured from film specimens and then coated with a ~5 nm Au/Pd overlayer to avoid charging during electron irradiation.

Thermogravimetric analysis

The thermal stability of the nanocomposites was analyzed by thermogravimetric analysis (TGA) using a Mettler TA-4000/TG-50 thermobalance coupled to a mass spectrometer, at a heating rate of 10ºC/min. Experiments were carried out on samples with an average mass of 10 mg, under dynamic conditions from room temperature to 700 ºC, in both oxidizing and inert atmosphere.

Differential scanning calorimetry

Dynamic DSC experiments were conducted in a Mettler TA4000 differential scanning calorimeter, equipped with a DSC-30 oven with automatic temperature control, operating under nitrogen flow. Samples of ~12 mg were heated at 380 ºC for 5 min, cooled to ambient temperature and then reheated to 380 ºC, both steps at a rate of 10 ºC/min. Glass transition temperatures were determined as the mid-point of the baseline shift, and the crystallization and melting temperatures were taken as the peak maxima or minima in the

calorimetric curves. The crystallinities can be estimated by the relation: $X_m = \Delta H_{m,PEEK} / (\Delta H°_{m,PEEK} \times w_{PEEK})$, where $\Delta H°_{m,PEEK}$ is the heat of fusion of an infinitely thick PEEK crystal[1] (~130 J/g), $\Delta H_{m,PEEK}$ is the apparent melting enthalpy of PEEK and w_{PEEK} is the weight fraction of the polymer matrix.

Dynamic mechanical analysis

The dynamic mechanical measurements of the samples (19.5 × 4 × 0.5 mm) were carried out using a Mettler DMA 861 dynamic mechanical analyzer. Experiments were performed in the temperature range between -130 to 250 ºC, at a heating rate of 2 ºC/min, in the tensile mode and at frequency of 1 Hz.

Tensile tests

The tensile properties of the nanocomposites were measured with an INSTRON 4204 mechanical tester at room temperature and 50 ± 5 % relative humidity. The strain rate was 1 mm/min under a load of 1 kN. Dog-bone specimens (Type V) were employed, as specified in the UNE-EN ISO 527-1 standard. All the samples were conditioned for 24 h before the measurements. The data reported are the average of the results of 6 specimens.

Electrical and thermal conductivity measurements

DC volume conductivity measurements were performed at ambient temperature on thin film samples (~10 × 10 × 0.2 mm) using a four-point probe (FPP) device (Scientific Equipment, India) with a spacing probe S = 0.2 cm. A constant current I was applied to the bar specimen through two outside probes with the help of a DC power supply (Model CCS-01) and the steady voltage V across the inside probes was measured with a digital microvoltmeter (Model DMV-001). The resistivity ρ was calculated through the

equation: $\rho = (\pi/ln\ 2)\ t\ (V/I)\ f_1\ f_2$, being t the thickness of the sample, f_1 and f_2 geometric correction factors.[2] The volume conductivity $\sigma = \rho^{-1}$ was obtained assuming that $f_1 \sim 1$ for $t << S$, and taking $f_2 = 0.76$ for the rectangular geometry of the specimens used.[3] To ensure reproducibility, 6 bars for each nanocomposite were tested.

Thermal conductivity experiments were carried out with a THASYS Hukseflux thermal sensor equipped with a thin heater (THA01) and a measurement and control unit (MCU). To eliminate the problem of contact resistance, thin film samples (~0.5 mm thick) were immersed in glycerol. Thermal conductivity values were calculated from the heat flux and the differential temperature across the samples. At least 3 specimens for each composition were tested to report an average value.

References

1. D. J. Blundell and B. N. Osborn, *Polymer,* 1983, **24**, 953.
2. V. S. Mironov, J. K. Kim, M. Park, S. Lim and W. K. Cho, *Polym. Test*., 2007, **26**, 547.
3. F. M. Smits, in *Measurement of Sheet Resistivities with the Four-Point Probe*, The Bell System Technical Journal, 1958, vol. 37, pp. 711-718.

Table S1. DSC thermal parameters of PEEK, the HPEEK-CNT sample and the different nanocomposites.

Sample (% CNTs)	T_c (ºC)	X_c (%)	T_m (ºC)	X_m (%)	T_g (ºC)
PEEK	309.1	42.5	344.2	44.8	147.5
HPEEK-CNT (7.8)	279.5	10.9	332.4	11.0	195.0
PEEK/CNT (0.1)	308.1	44.8	343.9	45.0	150.8
PEEK/CNT (0.5)	306.7	44.1	343.2	44.4	152.9
PEEK/CNT (1.0)	304.3	42.3	342.6	44.0	154.5
PEEK/HPEEK-CNT (0.1)	306.7	41.5	343.1	43.5	156.0
PEEK/HPEEK-CNT (0.5)	304.0	39.9	341.9	42.3	163.7
PEEK/HPEEK-CNT (1.0)	298.9	39.4	340.5	41.7	169.5

T_c and T_m are the crystallization and melting temperatures, respectively. X_c and X_m correspond to the crystallization and melting crystallinities. T_g is the glass transition temperature obtained from the heating thermograms.

Table S2. Characteristic degradation temperatures of PEEK nanocomposites obtained from TGA measurements under nitrogen atmosphere at a heating rate of 10 ºC/min.

Sample (% CNTs)	$T_{i,1}$ (ºC)	$T_{max,1}$ (ºC)	$T_{i,2}$ (ºC)	$T_{max,2}$ (ºC)	ΔT_2 (ºC)
PEEK	–	–	520	550	30
HPEEK-CNT-1 (7.8)	293	340	460	585	125
PEEK/CNT (0.1)	–	–	529	560	31
PEEK/CNT (0.5)	–	–	538	571	33
PEEK/CNT (1.0)	–	–	545	580	35
PEEK/HPEEK-CNT-1 (0.1)	339	393	541	578	37
PEEK/HPEEK-CNT-1 (0.5)	345	402	553	592	39
PEEK/HPEEK-CNT-1 (1.0)	350	405	574	614	40

T_i and T_{max} are the initial and maximum degradation rate temperatures, respectively. ΔT is difference between T_i and T_{max}. The subscripts 1 and 2 refer to the first and second stages.

Table S3. Storage modulus E´ at 25 ºC, glass transition temperature T_g, tan δ maximum value and area under tan δ peak for the different PEEK nanocomposites, obtained from dynamic mechanical analysis measurements at the frequency of 1 Hz.

Sample (% CNTs)	$E'_{25ºC}$ (GPa)	T_g (ºC)	Tan δ_{max} (a.u.)	$A_{tan\delta}$ (a.u.)
PEEK	3.83	148.0	0.173	5.10
HPEEK-CNT (7.8)	6.44	195.0	0.106	4.11
PEEK/CNT (0.1)	4.20	151.0	0.161	4.98
PEEK/CNT (0.5)	4.59	153.3	0.153	4.42
PEEK/CNT (1.0)	4.63	155.1	0.132	3.55
PEEK/HPEEK-CNT (0.1)	4.48	154.7	0.166	5.88
PEEK/HPEEK-CNT (0.5)	5.14	163.0	0.147	5.42
PEEK/HPEEK-CNT (1.0)	5.89	168.9	0.126	5.21