Supplementary Information

Morphology and thermal properties of novel poly(phenylene sulphide) hybrid nanocomposites based on single-walled carbon nanotubes and inorganic fullerene-like WS$_2$ nanoparticles

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Details of the characterization techniques

Scanning electron microscopy (SEM)

The dispersion of SWCNTs and IF-WS$_2$ in the PPS matrix was characterized using a Philips XL30 ESEM scanning electron microscope (SEM). Cryogenically fractured surfaces from film specimens were coated with a ~5 nm Au/Pd overlayer to avoid charging during electron irradiation.

Thermogravimetric analysis (TGA)

The thermal stability of the nanocomposites was analyzed by thermogravimetric analysis (TGA) using a TA Instruments Q500 thermobalance with a heating rate of 10ºC/min from room temperature to 700ºC under an inert atmosphere (nitrogen) with a flow rate of 150 ml/min.

Differential scanning calorimetry (DSC)

The crystallization and melting behaviour of the nanocomposites were investigated by differential scanning calorimetry using a Mettler TA4000/DSC30. The experiments were carried out in a nitrogen atmosphere with a flow rate of 30 ml/min using approximately 12 mg of sample sealed in aluminium pans. Prior to the cooling and

heating scans, the samples were held at 320 ºC for 5 min in order to erase the thermal history of the polymer. Then, the crystallization of the samples under non-isothermal conditions was carried out by cooling at 2, 5, 10, 15 and 20 ºC/min, followed by a heating cycle at 10ºC/min from 30 to 320ºC. The melting temperature (T_m) and the crystallization temperature (T_p) were determined at the maximum of the melting endotherm observed during the heating scan and the minimum of the crystallization exotherm observed during the cooling scan, respectively.

X-ray diffraction

Simultaneous small and wide angle x-ray diffraction (SAXS/WAXS) experiments using synchrotron radiation were performed at the A2 beamline of the HASYLAB synchrotron facility (DESY, Hamburg). Monochromatic x-rays of 0.15 nm wavelength were employed using a germanium single crystal as the dispersing element. The scattering was detected with a linear Gabriel detector. The sample to detector distance was 2360 mm for SAXS, and 135 mm for WAXS. The scattering angle of the SAXS pattern was calibrated with RTT (rat tail tendon), and that of the WAXS profile was calibrated with a highly crystalline PET standard. The maximum of the Lorentz-corrected SAXS diffractograms was used to calculate the long period ($L=1/s_{max}$) as a function of the temperature. L represents the sum of the average thickness of the crystal lamellae and of the interlamellar amorphous regions.

Thermal conductivity

The room temperature thermal diffusivity (α) of the samples was measured by a laser pulse method.[1] A Nd:YAG laser with wavelength of 1.06 μm was used to heat the front surface of a sample. A HgCdTe infrared detector with a response time of 40 ns and cutoff wavelength of 12.5 μm was employed for temperature detection. The data were collected with a 500 MHz bandwidth TDS3052B oscilloscope, and adjusted to the

Clark-Taylor model.[2] After calibration, the measurement error of the system was below ±5%. Since the thermal conductivity (λ) of the samples cannot be directly measured by the laser pulse method, λ was calculated according to the expression: $\lambda = \rho\, Cp\, \alpha$, where ρ and Cp are the density (as described previously) and the specific heat capacity of the samples, respectively. By assuming that the values of ρ and Cp for all the components are additive, the values for the nanocomposites can be estimated using the mixture rule. In particular, the Cp values used for PPS, CNTs and IF-WS$_2$ were 1.037 J/gK,[3] 0.6 J/gK[4] and 0.33 J/gK (this work), respectively. The experimental value of specific heat capacity of IF-WS$_2$ was determined from DSC analysis using STAR^e software and a standard reference of Al$_2$O$_3$ (Me-29595) by varying the temperature from -10 to 50ºC at 5ºC/min. Prior to the heating scans, the samples were held at -10ºC for 5 min.

Reference

1   W. J. Parker, R. J. Jenkins and C. P. Butler. *J. Appl. Phys.*, 1961, **32**, 1679.

2   L. M. J. Clark and R. E. Taylor. *J Appl. Phys.*, 1975, **46**, 714

3   Polymer Data Handbook, J. E. Mark ed., Oxford University Press, Oxford 1999, p. 714.

4   J. Hone, B. Batlogg, Z. Benes, A. T. Johnson and J. E. Fischer. *Science* 2000, **289**, 1730.

(a)

(b)
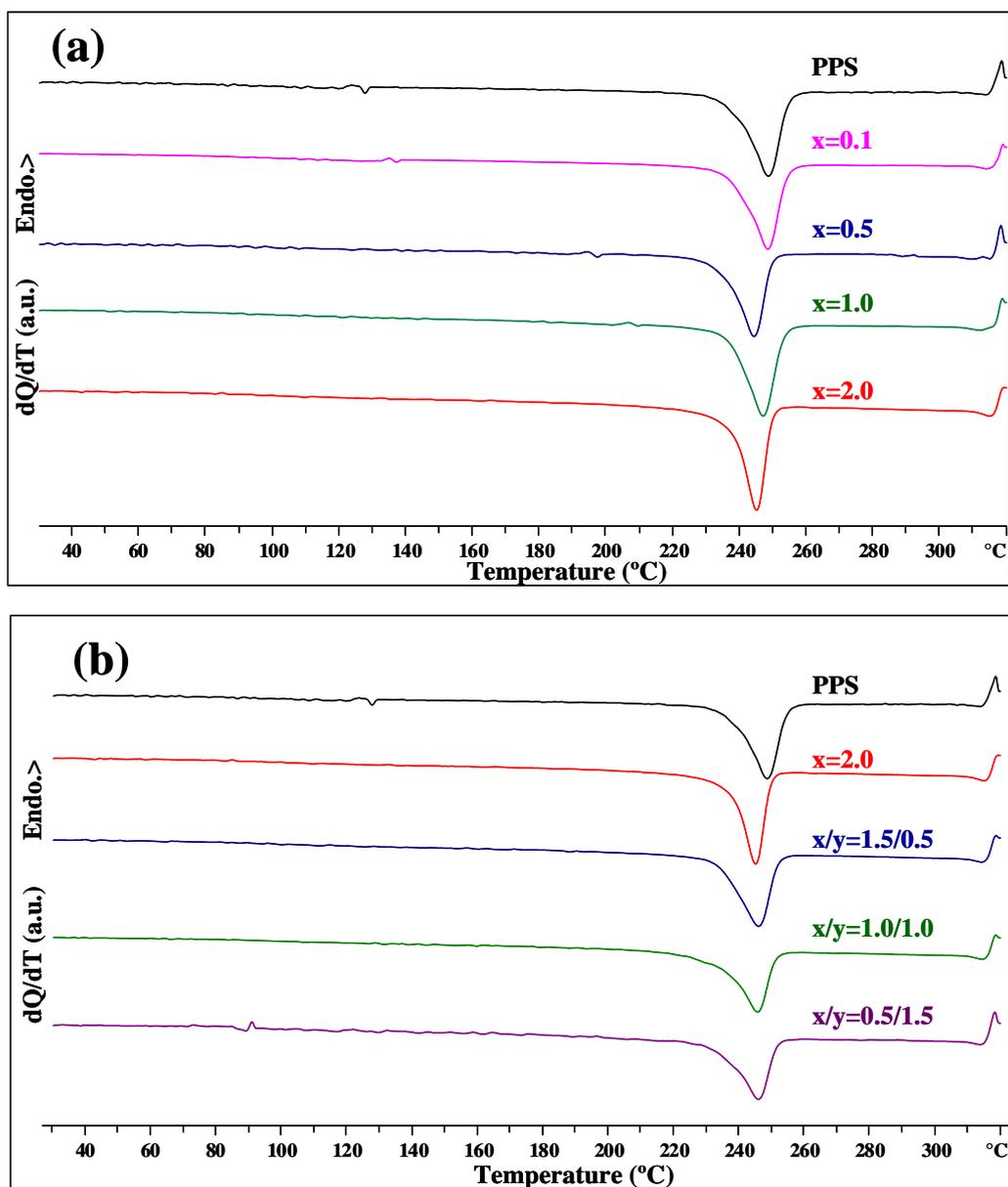
S1. DSC thermograms of dynamic crystallization of (a) PPS/SWCNT-PEI and (b) PPS/SWCNT-PEI/IF-WS$_2$ hybrid nanocomposites from melt to room temperature at 10ºC/min.

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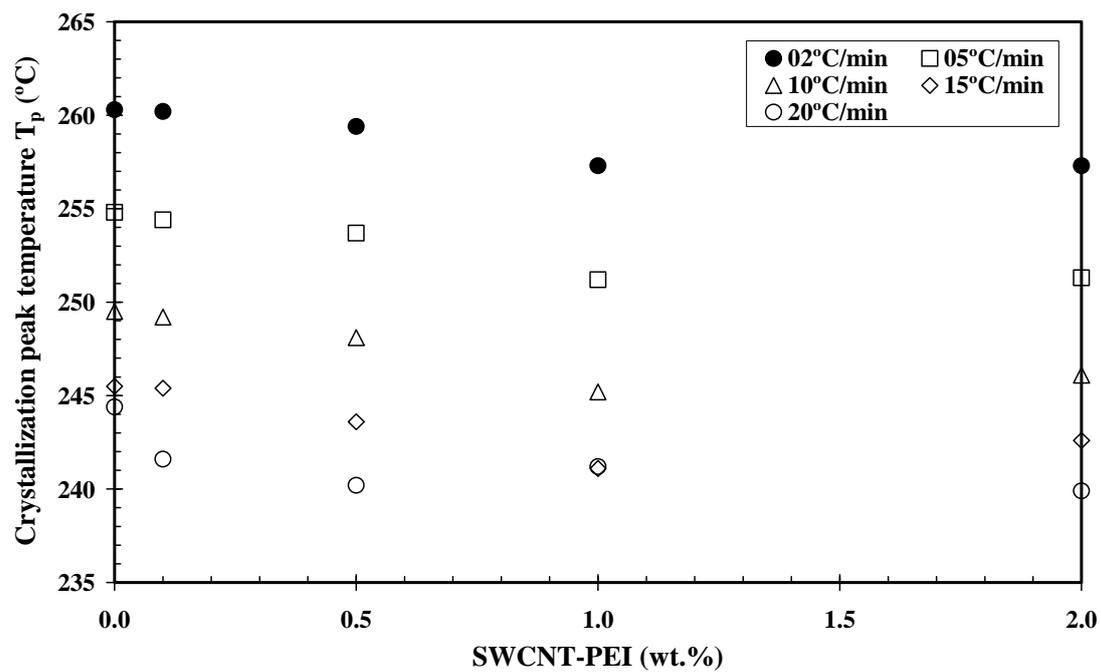
S2. Crystallization temperatures of PPS/SWCNT-PEI nanocomposites obtained at the cooling rates indicated.
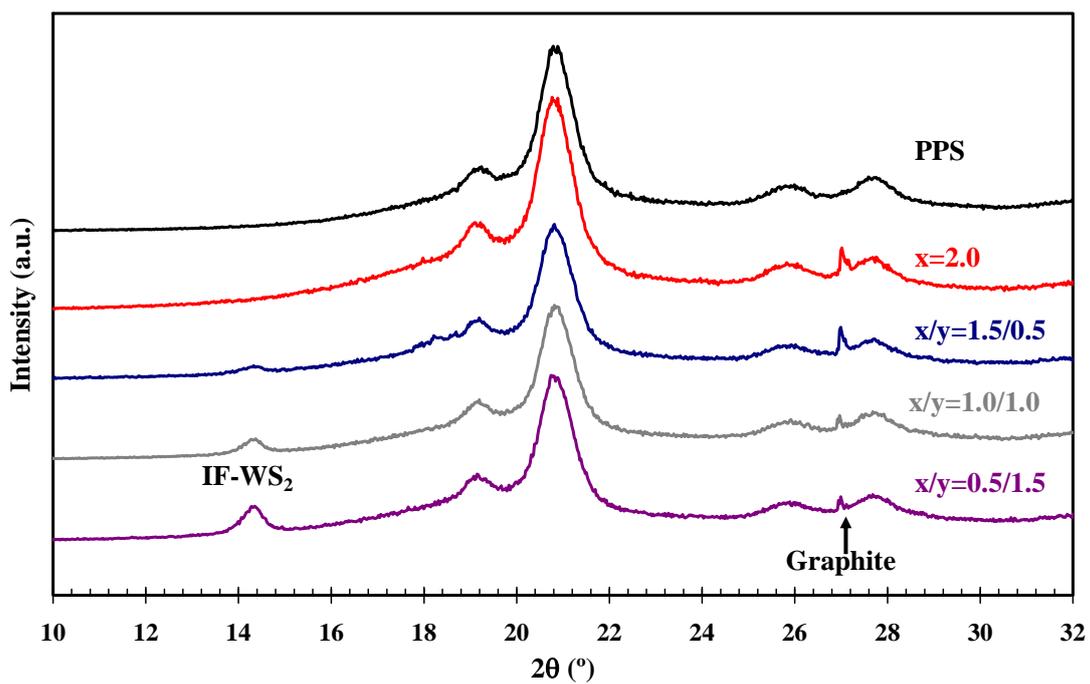
S3. WAXS diffractograms of melt-crystallized PPS/SWCNT-PEI/IF-WS$_2$ hybrid nanocomposites obtained at room temperature after cooling at 10ºC/min.

On the basis of the above results it was demonstrated that the addition of SWCNT-PEI(x) and IF-WS$_2$(y) does not influence the crystalline structure of PPS.
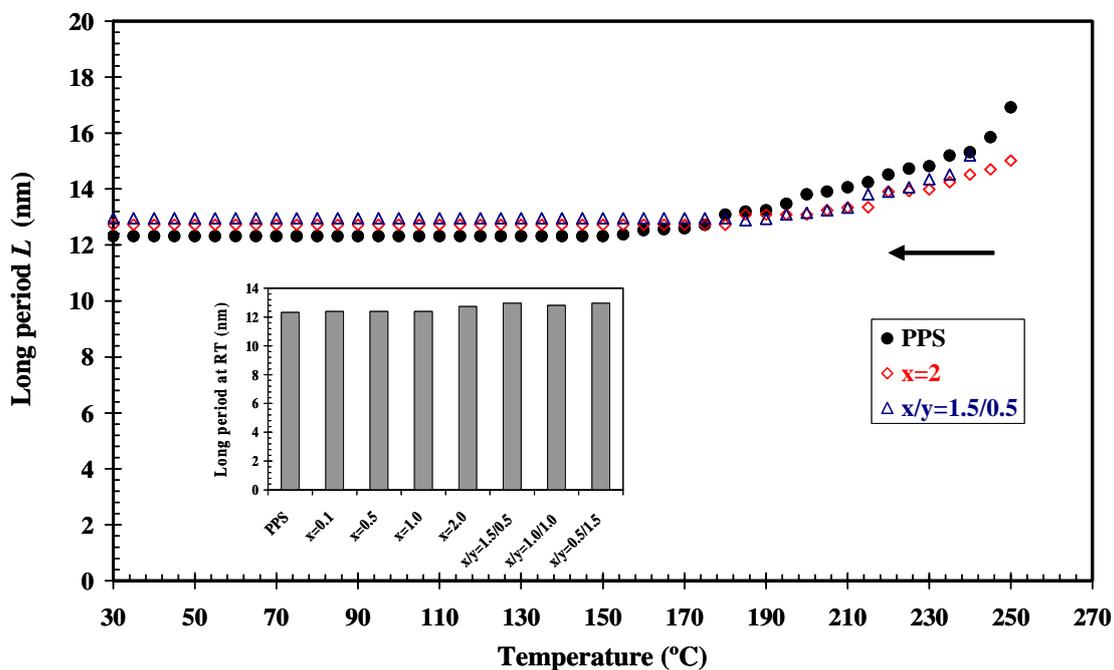
S4. Temperature-evolution of the long period (L) values of PPS/SWCNT-PEI/IF-WS$_2$ hybrid nanocomposites obtained during cooling at 10ºC/min; inset is the corresponding L values recorded at room temperature after dynamic crystallization.

On the same way, it was also demonstrated that the addition of SWCNT-PEI(x) and IF-WS$_2$(y) does not influence the evolution of the long period (L) values of PPS.