



Enhancing the thermomechanical behaviour of poly(phenylene sulphide) based composites via incorporation of covalently grafted carbon nanotubes



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ABSTRACT

The thermal and thermomechanical properties of poly(phenylene sulphide) (PPS) based nanocomposites incorporating a polymer derivative covalently anchored onto single-walled carbon nanotubes (SWCNTs) were investigated. The grafted fillers acted as nucleating agents, increasing the crystallization temperature and degree of crystallinity of the matrix. They also enhanced its thermal stability, flame retardancy, glass transition (T_g) and heat deflection temperatures while reduced the coefficient of thermal expansion at temperatures below T_g . A strong rise in the thermal conductivity, Young's modulus and tensile strength was found with increasing filler loading both in the glassy and rubbery states. All these outstanding improvements are ascribed to strong matrix-filler interfacial interactions combined with a compatibilization effect that results in very homogeneous SWCNT dispersion. The results herein offer useful insights towards the development of engineering thermoplastic/CNT nanocomposites for high-temperature applications.

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1. Introduction

One of the most important engineering thermoplastics is poly(phenylene sulphide) (PPS), a semicrystalline aromatic polymer composed of phenyl rings linked with sulphur atoms that possesses outstanding thermal and mechanical properties. It exhibits high decomposition temperature, good chemical, oxidation and flame resistance as well as high dimensional stability, minimum water absorption, anti-ageing and exceptional friction properties [1]. In addition, its low ionic content makes it an excellent electrical insulator. Extensive study has been carried out on this polymer. Several review articles covered most of the research topics about this material from synthesis and processing to characterization and modelling [2,3]. It is widely applied in many industrial fields, including the chemical, pharmaceutical, food, petroleum, electronics, automobile and aircrafts sectors. However, PPS has some limitations for certain applications requiring superior flame resistance, high glass transition temperature, strength or/and toughness. The addition of nanofillers into this thermoplastic is an attractive strategy to obtain composites with improved performance. For this purpose, different inorganic nanoparticles such as fullerene-like

tungsten disulphide (IF-WS₂) [4,5], Al₂O₃ [6] TiO₂, ZnO, and SiC [7] have been melt-blended with PPS matrix.

Over the past few years, integration of carbon nanotubes (CNTs) with excellent properties into polymers has become a greatly appealing route for fabricating advanced multifunctional materials [8]. One of the main advantages of using CNTs as fillers is their enormous surface area (several orders of magnitude larger than that of conventional fillers) that leads to an improved filler–matrix interfacial adhesion, a key factor to attain effective enhancement in the final properties of the composites. However, their huge surface area is also responsible for the strong tendency of the CNTs to form agglomerates that makes very difficult their dispersion within the matrix. To overcome these inconveniences, various methods have been developed, such as the modification of CNTs through covalent or non-covalent approaches [9]. The covalent bonding (grafting) of polymer chains to the CNT surface is the most preferred since results in strong polymer–CNT interfacial adhesion, hence large interfacial shear strength [10]. Further, the chemical nature of the anchored functional groups can generate a compatibilizing effect, thus improving the CNT dispersion in the polymer matrix; therefore, the properties of these nanocomposites are superior to those containing pristine CNTs.

Recently, a few works have been published on the preparation and characterization of PPS based composites incorporating pristine CNTs using conventional techniques such as compression

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[11,12], extrusion [13–15] or injection moulding [16]. Although these studies reported some improvements in the mechanical, electrical and wear performances, they were far below the expectations. More significant enhancements in the physical properties of this thermoplastic were found using non-covalent functionalization strategies such as the wrapping with polyetherimide [17–19] or maleimide polymers [20]. A more effective way to attain improved performance would be the formation of covalent linkages at the CNT–PPS interface; however, the insolubility of this polymer in common organic solvents and its lack of terminal end groups make difficult its functionalization, hence the grafting to other molecules. Therefore, studies dealing with the development of PPS/CNT nanocomposites through the covalent route are very scarce.

In a previous study [21], an aminated polymer derivative (PPS-NH₂) was covalently grafted onto the surface of acid-functionalized single-walled carbon nanotubes (SWCNT-COOH), and the experimental results demonstrated remarkable enhancements in the storage modulus, glass transition temperature and electrical conductivity of the polymer with the grafting process. The main aim of the present work is to investigate the effect of PPS-NH₂-g-SWCNT as fillers in a PPS matrix, particularly on the thermal and thermomechanical behaviour, comparing the results with those obtained for reference composites reinforced directly with the same amounts of acid-treated SWCNTs. The study of the thermal properties of PPS/PPS-NH₂-g-SWCNT nanocomposites such as crystallization behaviour, thermal stability, thermal conductivity and flame retardant performance is of a great interest for high-temperature applications as well as those requiring superior flame resistance or effective dissipation of accumulated heat. On the other hand, a detailed analysis of their thermomechanical properties including the glass transition temperature, coefficient of linear thermal expansion and heat deflection temperature is crucial for the design of nanocomposite structures where high dimensional stability and/or low distortion under load and temperature are required.

2. Experimental

2.1. Materials

PPS (Fortron 0205B4, $d_{25^\circ\text{C}} = 1.35 \text{ g/cm}^3$, $T_g \sim 90^\circ\text{C}$, $T_m \sim 280^\circ\text{C}$) was kindly provided by Ticona in powder form. The polymer was dried at 100°C for 14 h and stored in a dry environment before blending. The aminated derivative (PPS-NH₂) was synthesized from a nitrated PPS polymer using sodium dithionite (Na₂S₂O₄) as reduction agent [22]. CVD SWCNTs ($d_{25^\circ\text{C}} = 2.1 \text{ g/cm}^3$, diameter: 1–2 nm, length: 5–30 μm , amorphous carbon content $\leq 3 \text{ wt}\%$, purity $> 90\%$) were supplied by Cheap Tubes Inc, USA. They were oxidized in HNO₃ 6 M at 120°C for 4 h leading to acid-treated SWCNTs, and their functionalization degree ($\sim 7.1\%$) was determined from T_gA analysis. A detailed description of the grafting process of PPS-NH₂ onto the SWCNT-COOH is given elsewhere [21,23].

2.2. Preparation of PPS based nanocomposites

PPS-NH₂-g-SWCNT was initially mixed with the PPS powder by mechanical stirring and bath ultrasonication for approximately 30 min, and subsequently dried in vacuum at 50°C . PPS/PPS-NH₂-g-SWCNT nanocomposites with effective SWCNT contents in the range of 0.1–1.0 wt% were then prepared via melt-blending using a Haake Rheocord 90 extruder with counter-rotating screws. The rotor speed was set to 150 rpm and the processing temperature was kept constant at 320°C , with a mixing time of 20 min. For comparative purposes, similar nanocomposites reinforced

directly with the acid-treated SWCNTs were fabricated in the same way. Homogeneous films were manufactured by hot-compression at 320°C under successive pressure dwells of 5, 30 and 130 bars for 5 min at each pressure stage.

2.3. Characterization techniques

Scanning electron microscopy (SEM) images from cryo-fractured surfaces of the composites were obtained with a Philips XL30 microscope applying an acceleration voltage of 25 kV and an intensity of $9 \times 10^{-9} \text{ A}$.

Differential scanning calorimetry (DSC) experiments were carried out on a Mettler TA4000 differential scanning calorimeter, operating under nitrogen flow. Samples of $\sim 12 \text{ mg}$ placed in aluminium pans were melted at 320°C and kept at this temperature for 5 min to erase their thermal history. Subsequently, they were cooled from the melt to room temperature and then heated again up to 320°C at a scan rate of $10^\circ\text{C}/\text{min}$. The degree of crystallinity (X_c) was estimated according to the relation: $X_c = \Delta H_m / (\Delta H_m^\circ \times w_m)$, where ΔH_m° is the heat of fusion for a 100% crystalline PPS taken as 80 J/g [24], ΔH_m is the apparent melting enthalpy and w_m the weight fraction of the matrix.

Thermogravimetric analysis (TGA) experiments were conducted in a Mettler TA-4000/TG-50 thermobalance at a heating rate of $20^\circ\text{C}/\text{min}$. The temperature was scanned from 100 to 900°C under both oxidizing (air) and inert (nitrogen) atmospheres. Measurements were performed on samples of $\sim 20 \text{ mg}$ with a purge gas flow rate of $50 \text{ ml}/\text{min}$.

Tensile tests were carried out on a servo-hydraulic testing machine (type MTS 858) equipped with a temperature control system, using a crosshead speed of $1 \text{ mm}/\text{min}$ and a load cell of 100 kN , in the temperature range between 0 and 200°C , at $50 \pm 5\% \text{ RH}$. Experiments were performed according to the ASTM D638 standard. All the samples were conditioned for 24 h before the measurements. 5 coupons were tested for each sample, and the data reported correspond to the average value.

The heat release rate (HRR) was obtained by pyrolysis combustion flow calorimetry on samples of $\sim 10 \text{ mg}$. Prior to the measurements, samples were conditioned at $25 \pm 2^\circ\text{C}$ and $50 \pm 5\% \text{ RH}$ for 1 week. Experiments were carried out in a nitrogen stream at a heating rate of $60^\circ\text{C}/\text{min}$; the maximum pyrolysis temperature was 900°C . The decomposition products were mixed with excess oxygen and completely oxidized at high temperature. The HRR was determined by oxygen consumption calorimetry. All the composites were tested in triplicate to ensure good reproducibility.

The effective thermal conductivity (λ) was determined with a KES-F7 Thermo Labo type II equipment. The device is equipped with a temperature controlled hot plate, and is placed in a thermostatic chamber to be kept in a constant operating environment. The effect of the contact thermal resistance was removed by measuring the thermal conductivity of a reference material. λ was calculated using the equation $\lambda = t W / (T_{\text{hot}} - T_{\text{cold}}) A$, where t is the sample thickness, W is the heat flow, T_{hot} and T_{cold} are the temperatures of the hot and cold plates, respectively, and A is the surface area of the hot plate ($2.5 \times 2.5 \text{ mm}^2$). 5 specimens for each composite were tested and the average value is reported.

The coefficient of thermal expansion (CTE) was measured using a Perkin–Elmer TMA 7 thermomechanical analyzer. Samples of $\sim 7 \text{ mm} \times 7 \text{ mm}$ size were heated from 0 to 200°C at rate of $2^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. T_g was identified as the temperature at which the slope of the TMA plot changed, and the CTE was determined both below and above T_g .

Heat distortion temperature (HDT) was measured according to ASTM D648 standard using a TA 2980 DMA tester. Samples were conditioned at $25 \pm 2^\circ\text{C}$ and $50 \pm 5\% \text{ RH}$ for 48 h prior to the measurements. A constant load of 1.8 MPa was applied at the centre of

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