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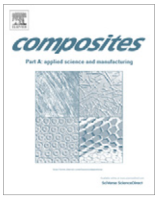

Poly(phenylene sulphide) and poly(ether ether ketone) composites reinforced with single-walled carbon nanotube buckypaper: I – Structure, thermal stability and crystallization behaviour

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ABSTRACT

Single-walled carbon nanotube (SWCNT) buckypaper (BP) reinforced-poly(phenylene sulphide) (PPS) and poly(ether ether ketone) (PEEK) composite laminates were manufactured through hot-press processing. Scanning and transmission electron microscopies were used for morphological characterization and qualitative evaluation of the impregnation degree of the BP. The thermal stability, resin and void content of the composites were evaluated through thermogravimetric analysis; a strong increase in the degradation temperatures of the polymers was found. Raman spectra revealed the existence of strong filler–matrix interactions. The glass transition temperature, crystallization and melting behaviour of the composites were investigated through differential scanning calorimetry and their crystalline structure was analyzed by wide angle X-ray diffraction. This investigation confirms that SWCNT-BPs can be used to fabricate high-loading CNT/thermoplastic composites with improved thermal properties.

1. Introduction

Over the last decades, carbon nanotubes (CNTs) have attracted considerable attention as reinforcement materials for polymer composites due to their extraordinary electrical, thermal and mechanical properties [1]. However, their low solubility in common solvents, strong agglomerating tendency and high viscosity of polymer/CNT mixtures caused a poor dispersion and limited their practical applications. To address these problems, CNT sheets, also known as "buckypapers" (BPs), have been recently used for the development of reinforced composites. BPs are free-standing porous mats of entangled CNT ropes cohesively bound by van der Waals interactions [2], commonly prepared by vacuum filtration through a membrane of a suspended solution of randomly distributed CNTs [3]. Many studies have been devoted to explore the potential applications of BPs, including supercapacitors, hydrogen storage materials, gas separators, electrodes, actuators, sensors and artificial muscles [4–7]. Several researches have tried to manufacture buckypaper composites by introducing the resin into the BP pores. Most of these studies have focused on epoxy/BP composites [8], which are of particular interest for the aeronautic industry. Nevertheless, thermoplastics such as polycarbonate (PC) [9], polyvinyl alcohol (PVA), polystyrene (PS), polyvinyl pyrrolidone (PVP) [10] or poly(ether ether ketone) (PEEK) [11] have also been used as polymer matrices.

The major differences between conventional polymer composites made of CNTs and those incorporating BPs are the carbon content, the bundle distribution and the manufacturing process. CNT-reinforced composites are usually prepared by melt-mixing [12], solution processing [13] or *in situ* polymerization [14]; their carbon content is generally lower than 5 wt.% and the CNT bundles are dispersed through the matrix without forming a network. In contrast, BP composites are manufactured by techniques such as hot-compression [11], electro-spinning [15], through-thickness infiltration [9] and intercalation [10]; they usually have a carbon content higher than 30 wt.%, resulting in a network which acts as an skeleton. In these composites, terms such as porosity, impregnation degree and quality of the interface BP-matrix are extremely important.

Poly(phenylene sulphide) (PPS) and PEEK are high-performance semicrystalline thermoplastic polymers that possess high thermal stability, chemical inertness, wear resistance and friction coefficient, excellent mechanical properties over a wide temperature range and low flammability [16,17]. These polymers can be processed by conventional techniques, such as extrusion and compression moulding, and applied as matrix resin for reinforced composites. They have been widely used in commercial and industrial fields, including electronics, automotive, aeronautic and chemical sectors [18]. Recently, we have demonstrated that the properties of these high-performance materials can be significantly enhanced by the integration of single-walled carbon nanotubes

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(SWCNTs) [19,20]. In particular, the addition of a small amount of SWCNTs wrapped in compatibilizing agents such as polyetherimide or polysulfone, led to a remarkable increase in the storage and Youngś modulus, T_g and degradation temperatures of the matrix [21,22]. However, the high aspect ratio of SWCNTs causes very high viscosity in melt, which negatively affects their uniform dispersion and also limits the loading, hence the potential improvement in properties.

When a semicrystalline polymer is modified by nanofillers, these can lead to improved or modified properties because of their influence on the final polymer structure. For example, the modulus, stiffness, hardness, yielding, optical and electrical properties are strongly dependent on the crystal size and crystalline structure, as well as on the degree of crystallinity. Therefore, in order to tailor the properties of the resulting material, special attention should be paid on the study of the structure and crystallization behaviour of the matrix in the composites. In this work, the thermal stability of SWCNT buckypaper-reinforced PPS and PEEK composite laminates manufactured through simple hot-press processing have been extensively investigated. Moreover, their crystallization and melting behaviour as well as crystalline structure have been thoroughly analyzed by differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXRD), respectively.

2. Experimental

2.1. Materials

PPS (Fortron 0205B4) was supplied by Ticona in powder form with an average particle size of 20 µm ($M_w \sim 30{,}000$ g/mol $d_{25^\circ C} = 1.35$ g/cm^3, $T_g \sim 90$ °C, $T_m \sim 285$ °C, $\eta_{310^\circ C} \sim 500$ Pa s). PEEK (150PF) was provided as fine powder by Victrex plc, UK ($M_w \sim 40{,}000$ g/mol, $T_g = 147$ °C, $T_m = 345$ °C, $d_{25^\circ C} = 1.30$ g/cm^3, $\eta_{350^\circ C} \sim 10^3$ Pa s). BioChar raw SWCNTs (purity about 70 wt.%) were synthesized using the two-laser oven technique [23]. The preparation of BP sheets from the laser-grown SWCNTs was made through vacuum filtration as described in our previous work [24]. The thickness of the BPs was in the range 60–80 µm, being the variation within each sheet lower than 2 µm. Their average areal weight and density were calculated to be 42 g/m^2 and 0.60 g/cm^3, respectively. Assuming a density of 1.3 g/cm^3 for SWCNT ropes, the average degree of porosity of the BP sheet was estimated to be 54%.

2.2. Manufacturing of buckypaper-reinforced composite laminates

Prior to compounding, PEEK, PPS and the SWCNT-BPs were placed in an oven at 120 ± 5 °C for 24 h to remove solvents and absorbed moistures. After drying, each polymer was extruded in a Haake Rheocord 90 system operating at 320 °C (PPS) or 380 °C (PEEK), with a rotor speed of 150 rpm for about 20 min. Subsequently, a small amount of the extruded material was used to fabricate films in a hot-press under successive pressures of 5, 40 and 130 bars for 6 min (PPS at 320 °C and PEEK at 380 °C). Steel shims were used to control the dimensions (~0.15 mm thick). Two flat brass plates were placed on both sides of the sample to obtain uniform thickness of the films. Kapton layers were used to prevent adhesion of the polymer to the plates.

The composites were prepared by placing a SWCNT buckypaper sheet between two PPS or PEEK films. Consolidation of the material was performed in a hot-press under high pressure, as shown in Fig. 1. The heating rate to the dwell temperature was ~5 °C/min, and the cooling to room temperature occurred slowly at a rate ⩽3 °C/min. The cycle steps were optimized to minimize the formation of internal pores and to improve the impregnation of the buckypaper with the polymer resin. The resulting laminates, with an average thickness of 0.22 mm, were cut into small specimens to be further used for the different characterizations.

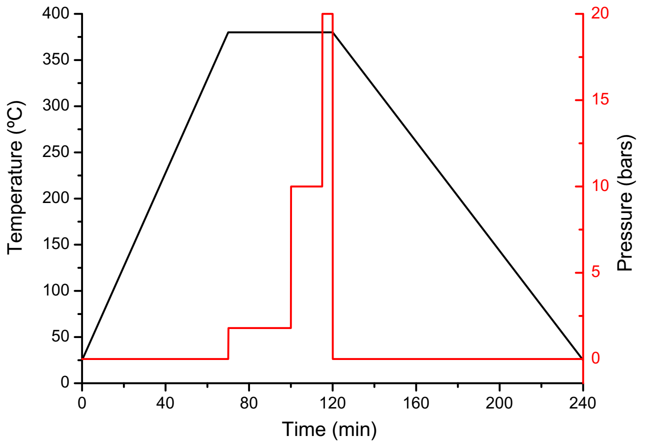

Fig. 1. Consolidation cycle used for the manufacturing of PEEK/SWCNT-BP laminates. A similar cycle with a dwell temperature of 320 °C was used for PPS based composites. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.3. Characterization techniques

2.3.1. Scanning and transmission electron microscopies

The surfaces of pristine BP and the composites were analyzed with a Philips XL30 scanning electron microscope (SEM), operating at 25 kV. Samples were coated with a ~5 nm Au/Pd overlayer to avoid charging during electron irradiation. For transmission electron microscopy (TEM), the specimens were embedded in a low viscosity epoxy resin (Spurr, Polysciences, Inc) under vacuum. Ultra-thin sections were cut using a Reichert Ultracut-S ultramicrotome equipped with a FCS cryo-device and placed on copper grids. TEM images were obtained with a Philips Tecnai 20 FEG (LaB6 filament) analytical electron microscope fitted with an EDAX detector, operating at 200 kV and with 0.3 nm point-to-point resolution.

2.3.2. Atomic force microscopy

AFM images were obtained on a Veeco Multimode Scanning Probe Microscope, using an antimony (*n*) doped silicon-tip cantilever with a nominal radius of 8 nm, resonance frequency of 330 kHz and spring constant of 42 N/m. Measurements were performed in the tapping mode in atmosphere environment; the scan rate was 0.426 Hz. Samples were prepared as thin films on silicon substrates.

2.3.3. Raman spectra

Raman spectra were acquired with an InVia Raman microscope (Renishaw), using a 785 nm (1.58 eV) laser excitation source and 50 × magnification objective lens. Spectra were recorded by scanning the 100–3000 cm^{-1} region, with a typical incident laser power of 0.5 mW, resolution of 4 cm^{-1} and total acquisition time of 3 min.

2.3.4. Differential scanning calorimetry

DSC experiments were conducted in a Mettler TA4000 differential scanning calorimeter, operating under nitrogen flow. Samples of ~12 mg were melted at 320 or 380 °C (for PPS or PEEK laminates, respectively), and maintained at this temperature for 5 min. Subsequently, they were cooled from the melt to room temperature at cooling rates of 2, 5, 10, 15 and 20 °C/min. Then, they were heated to the melting temperature at 10 °C/min. The crystallinity was