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Poly(ether ether ketone)-based hierarchical composites for tribological applications

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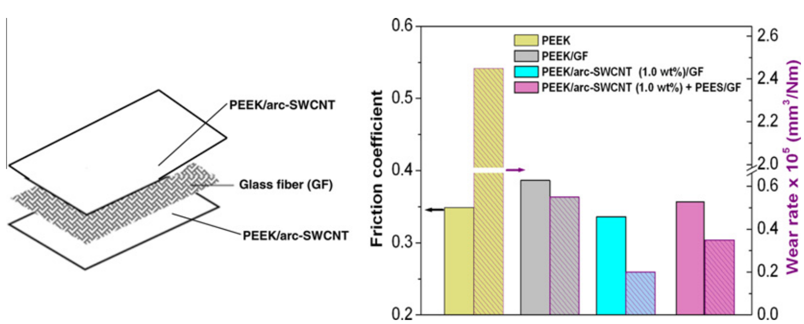
HIGHLIGHTS

- ▶ The tribological and rheological behavior of PEEK/SWCNT/GF laminates was studied.
- ▶ SWCNTs raised the viscosity, storage and loss moduli while decreased the wear rate.
- ▶ Composites with PEES as a compatibilizer showed higher viscosity and moduli values.
- ▶ Combination of both fillers led to synergistic effects on enhancing wear resistance.

GRAPHICAL ABSTRACT

PEEK/SWCNT/GF hybrid laminates were manufactured via extrusion and hot-compression. Compared to the neat matrix and binary PEEK/GF, the wear resistance was greatly enhanced.



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ABSTRACT

Poly(ether ether ketone) (PEEK)/glass fiber (GF) laminates reinforced with single-walled carbon nanotubes (SWCNTs) wrapped in poly(ether ether sulfone) (PEES) were manufactured by extrusion and hot-compression processes. The mechanical, tribological and rheological behavior of the hybrid composites and reference PEEK/SWCNT nanocomposites was analyzed. Viscoelastic measurements as a function of frequency ω revealed an increase in the complex viscosity, storage and loss moduli with the addition of the SWCNTs. Composites incorporating PEES as a compatibilizer exhibited higher moduli values and a smaller low-frequency slope of the storage modulus versus ω, indicating a more homogenous SWCNT dispersion. Moreover, they showed improved compression modulus and strength, suggesting a more effective matrix-SWCNT load transfer. The SWCNTs slightly lowered the friction coefficient of the composites while strongly decreased their wear rate. The compatibilizer reduced the lubricant effect of the SWCNTs and the heat dissipation during sliding, reflected in a smaller improvement in the tribological properties. SWCNT-reinforced laminates displayed outstanding wear behavior, attributed to their superior stiffness and strength, the lubrication capability of the SWCNTs, combined with a synergistic effect arising from the presence of the two types of fillers. The combination of conventional fibers with SWCNTs is a promising route to enhance the performance of the resulting hierarchical composites for tribological applications.

1. Introduction

Over the last decades, composites reinforced with carbon, graphite, glass or aramid fibers have been used for making tribological and structural components that encounter harsh operating conditions, such as high stresses, speeds and/or temperatures due

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to their superior performance combined with high stiffness, strength and weight reduction as well as excellent corrosion resistance. New opportunities arise by adding small amounts of nanofillers such as inorganic nanoparticles [1,2] or carbon nanotubes (CNTs) [3,4] to conventional fiber-reinforced polymers, leading to hierarchical composites with improved mechanical and wear behavior. This strategy is attractive since the mixing of several constituents enables the preparation of high-performance materials, due to a synergistic effect of both fillers on the enhancement of properties. A lot of effort in hierarchical composites has been focused on efficiently dispersing the nanofillers within the bulk matrix. For this purpose, a sonication step can be used to pre-disperse the nanofillers within the polymer prior to composite fabrication [5]. In the case of thermoplastic-based multiscale laminates, hot-press processing [1] is the method most frequently employed for integrating the fiber with the polymer/nanoparticle mixture.

Rheological studies of polymer based composites are interesting for improving processing conditions and understanding the microstructural changes occurring during processing. Melt rheology is a very sensitive method to characterize polymer melts; the presence of interconnected structures of fillers can lead to significant changes in the frequency dependence of the dynamic moduli and viscosity [6] at temperatures above the glass transition, related to percolation effects [7]. These changes have been interpreted as transitions from liquid-like to solid-like behavior, as reported for multi-walled carbon nanotube (MWCNT)-reinforced polycarbonate [6] or poly(ether ether ketone) (PEEK) [7] nanocomposites. While the melt rheology of short fiber-reinforced thermoplastic composites has been widely studied over the last years [8,9], reports on long fiber or fabric composites are very scarce [10]. On the other hand, tribological studies of composites are of great importance to utilize them in a wider range of applications, such as elements employed when problems of abrasion are particularly challenging. These properties are influenced by the morphology of the composite material in terms of degree of crystallinity, filler dispersion and orientation as well as by the filler-matrix interactions [11]. A complete study on the tribological performance is crucial to further exploit the potential of high-performance composites for technological applications involving friction and wear, usually at high temperatures. Material characteristics such as crystallinity, stiffness, hardness, impact strength, glass transition temperature, and surface energy, amongst others, are factors that strongly condition its sliding behavior. To improve the composite tribological properties, different strategies have been reported such as the incorporation of solid lubricants [12] or the addition of hard micro/nanoscale fillers [3,13].

PEEK is a semicrystalline engineering thermoplastic easily processed by a conventional extrusion technique that possesses excellent mechanical and thermal properties, high glass transition and melting temperatures, good tribological behavior, chemical, hydrolysis and radiation resistance, dimensional stability, low flammability and gas emission, etc. [14,15]. It has application in a variety of fields, ranging from medicine to the electronics, telecommunications, automobile and aeronautic industries [16,17]. Several studies have been reported on the tribological behavior of PEEK and its fiber composites. For example, Friedrich et al. [18] studied the friction and wear of PEEK/carbon fiber (CF) composites at different testing temperatures. Bijwe and Nidhi [19] investigated the mechanism of adhesive wear of PEEK reinforced with CF, glass fiber (GF) and solid lubricants (polytetrafluoroethylene (PTFE) and graphite); the addition of fibers was found to be beneficial for improving both the strength and wear resistance of this polymer. Further, a few works on the tribological properties of PEEK nanocomposites with carbon nanoparticles have been reported [20–24]. However, to the best of our knowledge, there is no previous study dealing with the tribological behavior of single-walled carbon nanotube (SWCNT)-reinforced PEEK/GF hybrids.

In the present study, SWCNT-reinforced PEEK/GF laminates were fabricated via extrusion and hot-press processing. To improve the distribution of the nanotubes and the polymer/SWCNT affinity while preserving the integrity of the tubes, poly(ether ether sulfone), PEES, was used as a compatibilizing agent [25]. The influence of the SWCNTs and the polymer wrapping on the viscoelastic properties, mechanical performance, friction and wear behavior of the resulting hierarchical composites was analyzed, and the results were correlated with the microstructure of the materials and compared with those of PEEK/SWCNT nanocomposites.

2. Experimental section

2.1. Materials

PEEK 150PF grade was provided in fine powder form by Victrex plc, UK ($M_w \sim 40000$ g/mol, $T_g = 147$ °C, $T_m = 345$ °C, $d_{25°C} = 1.30$ g/cm^3). Arc-grown SWCNTs were synthesized at the Institute of Carboquimica (ICB-CSIC) using graphite electrodes and Ni/Y$\sim$4/1 atomic% as catalyst, and purified by thermal treatment in air atmosphere at 350 °C for 2 h followed by reflux in HCl 3 M for 2 h; this process introduces functional groups (mainly COOH) on their sidewalls. Poly(1–4-phenylene ether–ether sulfone), PEES ($M_w \sim 38{,}000$ g/mol, $T_g = 192$ °C, $d_{25°C} = 1.38$ g/cm^3), was supplied by Sigma–Aldrich in pellet form. A detailed description of the wrapping process of the arc-SWCNTs in PEES is given in our previous work [26]. Briefly, 25 mL of a PEES 1-methyl-2-pyrrolidone (NMP) solution (1.5% w/w) were mixed with $\sim$260 mg of SWCNTs with bath sonication for 5 min. Each mixture was treated with an ultrasonic tip for 60 min, filtered with a PTFE membrane, dried under vacuum at 60 °C during 24 h and finally milled in an agate mortar. E-glass plain weave fiber fabric (TG09P) was purchased from JB Martin, Canada (areal density of 0.02821 g/cm^2, $d_{25°C} = 2.50$ g/cm^3).

2.2. Preparation of PEEK/SWCNT/GF laminates

The melt-blending of the PEEK powder and the SWCNTs (either wrapped or non-wrapped) was performed in a Haake Rheocord 90 extruder operating at 380 ± 5 °C, with a rotor speed of 150 rpm, using mixing times of 20 min. A SWCNT concentration of 1.0 wt.% was selected based on a compromise between achieving good dispersion and maximizing mechanical properties [15]. The PEEK/SWCNT extrudate was used to fabricate thin films ($\sim$0.5 mm thick) by hot-compression, under successive pressure dwells of 5, 40 and 130 bars, for periods of 6 min at each pressure, and the resulting nanocomposites were taken as reference samples.

The laminates were prepared by alternatively placing 4 plies of glass fabric within 5 PEEK/SWCNT films. Consolidation of the material was made in a hot-press at 380 ± 5 °C under three consecutive pressure steps of 10, 40 and 130 bars, which were optimized to improve fiber impregnation. The heating rate to the dwell temperature was about 5 °C/min and the cooling to room temperature was performed slowly at a rate of $\sim$3 °C/min. The resulting laminates had a matrix content of 36 ± 1 wt.%, a fiber content of 63 ± 1 wt.% and an average density of 1.82 ± 0.04 g/cm^3. The density of laminate coupons at 20 °C was obtained using a specific gravity determination kit equipped with a Sartorious 6080 electronic balance (readability of 0.001 mg) [27]. The values were calculated based on the Archimedes' principle according to the equation $\rho_c = [w_a/(w_a - w_w)] \times \rho_o$, being ρ_c the density of the specimen, w_a and w_w the weight of the specimen in air and water, respectively, and ρ_o the density of the water at that temperature.