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Mechanical and thermal behaviour of isotactic polypropylene reinforced with inorganic fullerene-like WS_2 nanoparticles: Effect of filler loading and temperature

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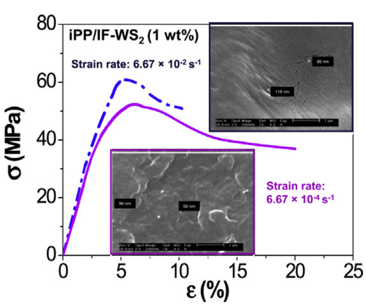
HIGHLIGHTS

- The thermal and mechanical behaviour of iPP/IF-WS_2 nanocomposites was studied.
- Low IF-WS_2 contents provide a good balance between stiffness, strength and toughness.
- Their tensile behaviour is sensitive to the strain rate and temperature.
- The nanocomposites exhibit superior thermal conductivity and flame retardancy than iPP.
- The benefits of using IF-WS_2 compared to other nanoscale fillers are highlighted.

GRAPHICAL ABSTRACT



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ABSTRACT

The thermal and mechanical behaviour of isotactic polypropylene (iPP) nanocomposites reinforced with different loadings of inorganic fullerene-like tungsten disulfide (IF-WS_2) nanoparticles was investigated. The IF-WS_2 noticeably enhanced the polymer stiffness and strength, ascribed to their uniform dispersion, the formation of a large nanoparticle–matrix interface combined with a nucleating effect on iPP crystallization. Their reinforcement effect was more pronounced at high temperatures. However, a drop in ductility and toughness was found at higher IF-WS_2 concentrations. The tensile behaviour of the nanocomposites was extremely sensitive to the strain rate and temperature, and their yield strength was properly described by the Eyring's equation. The activation energy increased while the activation volume decreased with increasing nanoparticle loading, indicating a reduction in polymer chain motion. The nanoparticles improved the thermomechanical properties of iPP: raised the glass transition and heat deflection temperatures while decreased the coefficient of thermal expansion. The nanocomposites also displayed superior flame retardancy with longer ignition time and reduced peak heat release rate. Further, a gradual rise in thermal conductivity was found with increasing IF-WS_2 loading both in the glassy and rubbery states. The results presented herein highlight the benefits and high potential of using IF-nanoparticles for enhancing the thermomechanical properties of thermoplastic polymers compared to other nanoscale fillers.

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1. Introduction

Polypropylene (PP) is a semicrystalline commodity plastic widely used in food packaging, medical care, automobile and other industrial sectors due to its low cost, easy processability, low density and well-balanced physical and mechanical properties like ductility and strength at room temperature and/or under moderate rates of deformation [1]. Nevertheless, under severe conditions it becomes brittle. A wide number of microfillers including mica, silica, alumina, talc, glass fibre, carbon black, etc [2–4] have been incorporated into PP to further improve its mechanical properties and simultaneously increase its longevity and durability, thus fulfilling the requirements for certain engineering applications. However, large amounts of these microfillers (20–30 wt%) are required to attain significant property enhancements, which has detrimental effects on the processability of the composites, increases cost and weight.

On the other hand, nanoparticle reinforced polymers are attracting a lot of attention in recent years due to their unique properties resulting from the nanoscale structures. The exceptionally high nanoparticle specific surface area enables the formation of a large interphase in the nanocomposite and strong nanofiller–matrix interactions. Thus, the addition of nanometric fillers such as montmorillonite clays [5], $CaCO_3$ [6], SiO_2 [7], carbon nitrides [8], or carbon nanotubes (CNTs) [9,10] to PP has been reported to improve significantly the Young's modulus and yield stress. For example, the incorporation of very low loadings (0.25 wt%) of single-walled carbon nanotubes (SWCNTs) led to a remarkable increase in stiffness and strength, by ca. 20%, albeit these properties were found to decrease at higher concentrations due to the formation of SWCNT aggregates. Therefore, a lot of effort is now focused on the design of novel strategies to prepare nanocomposites with optimal nanofiller dispersion. Amongst the most promising types of nanoreinforcements are inorganic nanoparticles of layered metal dichalcogenides such as WS_2 and MoS_2 [11] that possess similar structure to fullerenes. These non-carbon materials are named as inorganic fullerene-like (IF) nanoparticles and exhibit outstanding properties like very high stiffness and strength [12]; they are strong enough to withstand uniform pressures up to 21 GPa. This superior mechanical performance is ascribed to their small size (typically in the range of 40–180 nm), quasi-spherical shape, closed-cage layered structure and chemical inertness. Moreover, they are cheaper than organic nanofillers (i.e. CNTs, nanofibers, graphene), more environmentally friendly and display lower agglomerating tendency, hence can be homogenously dispersed within polymer matrices without the aid of surfactants or compatibilizing agents [13,14]. Further, the IF nanoparticles have excellent solid lubricant behaviour, and their efficiency as lubricant additives for improving the tribological properties of epoxy [15] and thermoplastic polymers [16,17] has been recently demonstrated.

Polymer matrix composites (PMCs) are commonly used in a wide variety of engineering applications such as aircraft, automotive and construction components, in which they are frequently subjected to different temperatures and dynamic loadings. In order to avoid any mishap during service, it is crucial to investigate the deformation behaviour of PMCs over a range of strain rates and temperatures, analyzing the influence of parameters such as filler size, quantity, shape and geometry as well as the interactions between fillers and matrix that play a major role in determining the overall mechanical performance. Previous works on strain rate deformation behaviour have primarily focused on neat polymers [18,19] and their microcomposites [20,21]. However, there exists little information available regarding the effects of temperature and deformation rate on the yield strength of thermoplastic based nanocomposites [22], particularly those reinforced with inorganic nanoparticles [23]. Thus, this is a great opportunity to ascertain the capabilities and possibilities of nanocomposites to replace conventional materials, especially in high temperature/strain rate applications.

In a previous work [14], isotactic polypropylene (iPP)/IF-WS_2 nanocomposites with various nanofiller loadings were prepared via traditional melt-blending process, and the experimental data demonstrated a remarkable enhancement in the thermal stability as well as an increase in the crystallization rate of the matrix when compared with neat iPP. The aim of the current study is to show the advantages of using IF nanoparticles as a suitable alternative for other inorganic and organic nanofillers that have been used for enhancing the mechanical and thermal properties of PP. To achieve this goal, the effect of IF-WS_2 content, strain rate and temperature on the Young's modulus, yield strength, tensile elongation and toughness of this thermoplastic matrix has been explored in detail, and the results have been compared to those reported for iPP/CNT and iPP/SiO_2 nanocomposites. Further, the influence of the IF nanoparticles on different thermomechanical properties including the coefficient of thermal expansion (CTE), heat deflection temperature (HDT) and glass transition temperature (T_g) as well as on the thermal behaviour like flammability and thermal conductivity is analyzed.

2. Experimental section

2.1. Materials and processing

iPP was supplied by Repsol-YPF (Spain), with 95% isotacticity, a viscosity average molecular weight of 179,000 g mol^{-1} and a polydispersity of 4.77. Inorganic fullerene-like tungsten disulfide (IF-WS_2) nanoparticles (NanoLub™, $d_{25\,^\circ C}$ ~7.5 g cm^{-3}) were provided by Nanomaterials (Israel). A detailed morphological study of these nanomaterials using SEM was carried out in the preceding work [14]. They are closed-cage hollow multilayered polyhedral nanoparticles with a shape ranging from spheres to ellipsoids. The particle aspect ratio ranges between 1 (spheres) and 2.3, with a mean value of 1.4 and a standard deviation of 0.3. Most of the nanoparticles display quasi-spherical shape with diameter in the range of 40–180 nm (mean value of 80 nm). They have an onion-like structure and are composed of concentric WS_2 layers evenly spaced by 6.18 Å. Its hollow nature is reflected by the contrast difference in the core, and the dimension of the hollow void in the centre is about half the overall nanoparticle diameter. The iPP/IF-WS_2 nanocomposites (0.05–8.0 wt% nanoparticle loading) were prepared via melt-blending in a Haake Rheocord 90 extruder operating at 210 °C, with mixing times of 10 min and a rotor speed of 150 rpm. Subsequently, a small amount of the extruded material was used to fabricate films in a hot-press at 210 °C under successive pressures of 10, 50 and 120 bars during 2 min at each pressure.

2.2. Materials characterization

Tensile tests were carried out on a servo-hydraulic testing machine (type MTS 858) equipped with a controlled temperature chamber at 23, 35, 50, 65 and 80 °C. Dog-bone tensile coupons were employed, according to the ASTM D638 standard. Specimens were conditioned at the testing temperature and 50 ± 5% RH for 24 h prior to the measurements. The cross-head speeds applied were in the range of 1–100 mm min^{-1}, corresponding to relative strain rates between 6.67×10^{-4} and 6.67×10^{-2} s^{-1}. Five specimens at each cross-head speed and fixed temperature were tested for each sample, and the data reported correspond to the average value. The fractured surfaces of tensile coupons of iPP and the nanocomposites were observed using a Philips XL30 scanning electron microscope