

## Preparation and properties of polyimide nanocomposites with negative thermal expansion nanoparticle filler

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### H I G H L I G H T S

- ▶ Polyimide nanocomposites with nanoparticles of zirconium tungstate were prepared.
- ▶ Effect of surface functionalized ZrW<sub>2</sub>O<sub>8</sub> on properties of nanocomposites is reported.
- ▶ Polyimide–ZrW<sub>2</sub>O<sub>8</sub> nanocomposites exhibit reduced CTE and increased tensile modulus.
- ▶ The CTE of polyimide is reduced by 22% with the addition of 15 volume% ZrW<sub>2</sub>O<sub>8</sub>.
- ▶ Surface functionalization of filler improves the tensile properties of composites.

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### A B S T R A C T

Nanocomposites with tunable coefficient of thermal expansion (CTE) were prepared by incorporating cubic zirconium tungstate (ZrW<sub>2</sub>O<sub>8</sub>) nanoparticles at various volume percentages in a polyimide (PI). Rod-shaped nanoparticles of cubic ZrW<sub>2</sub>O<sub>8</sub>, which has isotropic negative thermal expansion, were synthesized using a hydrothermal method. The interfacial interaction between the PI and ZrW<sub>2</sub>O<sub>8</sub> was enhanced by covalently bonding different organic moieties, including a short aliphatic silane and PI oligomer, to the surface of ZrW<sub>2</sub>O<sub>8</sub>. Structure–property relationships for the PI–ZrW<sub>2</sub>O<sub>8</sub> nanocomposites were investigated for thermal degradation, glass transition, tensile and thermal expansion properties. Addition of ZrW<sub>2</sub>O<sub>8</sub> nanoparticles did not alter the thermal degradation and glass transition temperature of the base PI. The addition of ZrW<sub>2</sub>O<sub>8</sub> nanoparticles increased the Young's modulus of the polymer, indicating stiffening of the polyimide matrix. The increase was higher for nanocomposites with engineered interfaces due to the efficient load transfer achieved through the presence of linker groups. The addition of ZrW<sub>2</sub>O<sub>8</sub> reduced the in-plane CTE of the base PI at all loadings studied. The CTE of the base PI was reduced by around 22% with the addition of ZrW<sub>2</sub>O<sub>8</sub> at 15 volume% loading.

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## 1. Introduction

Polymers expand considerably with increase in temperature compared to metals and ceramics. Since polymers are used as coatings on metals and ceramics in a variety of applications, the mismatch in the coefficient of thermal expansion (CTE) of polymers and metals/ceramics causes delamination and material failure, and limits the use of polymers especially at higher temperatures. For example, aromatic polyimides (PI) have a considerably higher linear CTE (40–80 ppm K<sup>-1</sup>) compared to ceramics and metals (Cu: 16–18 ppm K<sup>-1</sup>, SiO<sub>2</sub>: 14 ppm K<sup>-1</sup>, Si: 3–5 ppm K<sup>-1</sup>).

Aromatic PIs are widely used as high performance polymers in industrial applications including electronics, coatings, aerospace and gas separations [1,2]. Excellent thermal and mechanical stability, good chemical resistance, low water absorption and low dielectric constants make PIs suitable as dielectric interconnects, membranes, composites, protective coatings and adhesives [3–5]. Although PIs are widely used in high temperature applications, the high CTE of PIs limits their use for some applications. This has led to a significant research interest in developing PIs with lower inherent CTEs [6–12]. While developing PIs with low CTEs is the objective, it is also essential to maintain other favorable bulk properties of the polymer.

Formation of a linear polymer backbone with rigid-group molecular structures [6–9] and addition of a filler with low CTE

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[10–14] to the polymer are the most common approaches used to reduce the CTE of PIs. The rigid groups within the polymer backbone result in low in-plane CTE, but often cause reduced flexibility and processability compared to the original polymers, leading to failure under mechanical stress [7]. In addition, the design and synthesis of new monomers and PIs are expensive and tedious. Incorporation of fillers with low CTE in polymers to form composites is a preferred approach to reduce the thermal expansion of polymers. In particular, addition of “nano” fillers is an attractive way to lower the CTE of polymers without losing the inherent bulk properties of the polymer [10–17].

Polymer based composites with reduced CTE have been prepared using nanofillers that exhibit low positive CTE or negative CTE such as polyhedral oligomeric silsesquioxanes [10,11], montmorillonite nanoclay [12,15,16], silica [13], silicon nitride [14], and cubic zirconium tungstate [17]. The fillers reduce the CTE because of both their inherent low CTE and the increase in the stiffness of the polymer chains due to the presence of rigid fillers. While incorporating low positive CTE fillers in polymers can reduce the overall CTE, fillers exhibiting negative thermal expansion (NTE) hold promise to achieve a more significant reduction of CTE in the nanocomposites. Theoretical CTE predictions of polymer nanocomposites using a simple model such as the rule of mixtures show that the NTE fillers can lower the CTE of the polymer more than positive CTE fillers at any given filler loading. This has resulted in an increasing interest for using fillers that exhibit isotropic NTE. Cubic zirconium tungstate ( $ZrW_2O_8$ ) is expected to have excellent potential to reduce the CTE of polymers because of its isotropic negative thermal expansion (NTE) behavior over a wide temperature range (CTE =  $-9 \text{ ppm } ^\circ\text{C}^{-1}$  from  $-272 \text{ }^\circ\text{C}$  to  $155 \text{ }^\circ\text{C}$  and  $-5 \text{ ppm } ^\circ\text{C}^{-1}$  from  $155 \text{ }^\circ\text{C}$  to  $777 \text{ }^\circ\text{C}$ ). Several studies have reported  $ZrW_2O_8$  based composites with reduced CTE as compared to the original starting material [17–25]. Tani et al. [23] reported a reduction in CTE from  $46.3 \text{ ppm } ^\circ\text{C}^{-1}$  to  $14.3 \text{ ppm } ^\circ\text{C}^{-1}$  when the  $ZrW_2O_8$  volume increased from 0 to 50 volume% in a phenolic resin matrix. Miller et al. [24] showed that  $ZrW_2O_8$  modified with carboxylic acid at 40 volume% loading in an epoxy matrix reduced the CTE by 50% as compared to the base polymer. Most of the reported studies have been confined to conventional composites with micron size oxide particles. As several fillers at nanoscale have been proven to impart value-added properties to the polymer compared to their micron size counterparts [26,27], it is of interest to study the effect of  $ZrW_2O_8$  nanoparticles on the bulk properties of polymers including thermal expansion. Sullivan et al. [17] incorporated nano and micron particles of  $ZrW_2O_8$ , synthesized by a sol-gel route, to reduce the CTE of a stiff PI matrix. At lower filler loadings (1.7 volume%), CTEs of composites with nano and micron particles of  $ZrW_2O_8$  were comparable. Although the reduction in the filler particle size did not alter the CTE of the composites, further investigation is required to understand the effect of filler particle size on the mechanical properties of composites. In addition, recent progress in synthesizing nanoparticles of  $ZrW_2O_8$  with controlled size and morphology [28–31] has also resulted in renewed interest in studying polymer- $ZrW_2O_8$  nanocomposites [32–35].

Efforts to produce PI nanocomposites using cubic  $ZrW_2O_8$  nanoparticles are discussed in this paper. The novelty of this work is the engineering of the PI- $ZrW_2O_8$  interface with a linker group that not only promotes the polymer-filler adhesion (e.g., silane), but can potentially entangle with the polymer backbone and work in synergy with  $ZrW_2O_8$  to reduce the CTE of the polymer. This can be achieved by using longer groups such as PI oligomers to functionalize the interface as shown in Fig. 1. As the filler particle contracts with an increase in temperature, the long interfacial groups bridging the polymer and  $ZrW_2O_8$  could help in transferring the

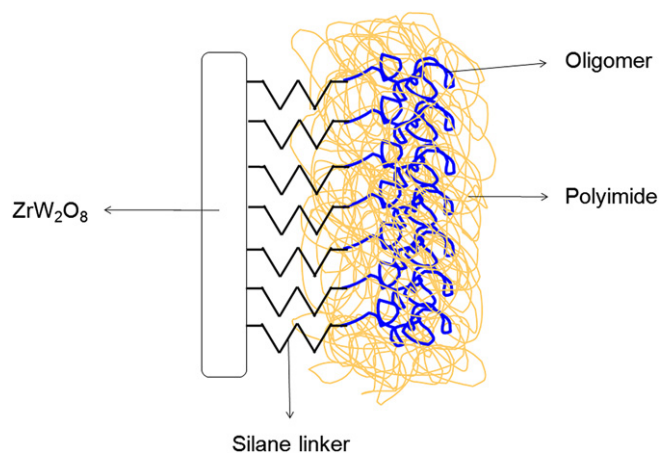


Fig. 1. Schematic representation of PI- $ZrW_2O_8$  interfacial engineering.

NTE behavior of the filler to the polymer, which may provide a second mechanism for reducing the CTE of the polymer.

While functionalization of nanofillers improves the filler dispersion in the polymer matrix, optimized processing strategies are essential to ensure homogenous dispersion of nanofiller particles in the polymer matrix. Sonication [36], homogenization, ball-milling [37], melt mixing and in-situ polymerization [38] are examples of processes commonly used to improve the dispersion of nanofillers in the polymer matrix. A modified solvent casting process was used to prepare composite samples for this study. Specifically, for “reprecipitation blending”, a sonicated solution of the nanofiller was added to hot polymer solution followed by precipitation of the polymer-nanofiller mixture into a non-solvent. The expansion of polymer coils in a high temperature solvent, and the precipitation of the polymer-filler mixture, can allow physical wrapping of the nanofillers with the polymer chains and improved dispersion in the composite [39,40]. The effect of loading and surface chemistry on the nanofiller dispersion, thermal-mechanical properties and thermal expansion coefficient of  $ZrW_2O_8$ -polyimide composites are reported.

## 2. Experimental

### 2.1. Materials

LaRC-CP1, a fluorinated PI developed by NASA Langley Research Center and purchased from ManTech SRS Technologies, was used as the polymer matrix for the nanocomposites in this study. The fluorinated groups present in LaRC-CP1 from the diamine and dianhydride monomers, as shown in Fig. 2, provide a low dielectric constant, exceptional thermal stability, and optical transparency for the polymer [8], making this PI ideal for industrial applications.

The starting materials and reagents required for  $ZrW_2O_8$  synthesis were zirconium oxychloride ( $ZrOCl_2 \cdot xH_2O$ ) (Alfa Aesar), sodium tungstate ( $Na_2WO_4 \cdot 2H_2O$ ) (Strem Chemicals), perchloric acid ( $HClO_4$ ) (Alfa Aesar), sodium chloride (NaCl) (Fisher Scientific) and deionized water. *N,N*-Dimethylacetamide (DMAc) (Sigma-Aldrich), 3-aminopropyltriethoxysilane (APTES) (Gelest), acetone

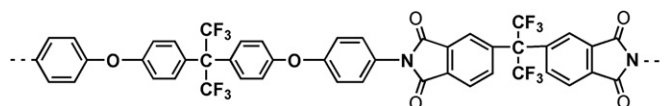


Fig. 2. LaRC-CP1 polyimide repeat unit.

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