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Fabrication and properties of polyimide composites filled with zirconium tungsten phosphate of negative thermal expansion

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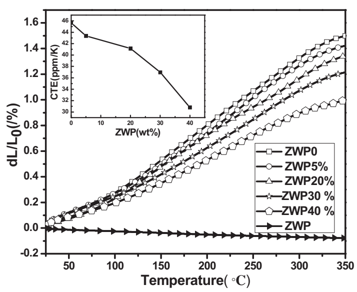
HIGHLIGHTS

- $Zr_2P_2WO_{12}$ was firstly used as filler to tune the TEC of polyimides.
- The TECs of polyimides were reduced by introduction of $Zr_2P_2WO_{12}$ powders.
- Polyimides with reduced TECs have favorable thermal and dielectric properties.

GRAPHICAL ABSTRACT



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ABSTRACT

Negative thermal expansion $Zr_2WP_2O_{12}$ (ZWP) powder prepared by hydrothermal method was used as fillers to tailor the thermal expansion coefficient (TEC) of the polyimide (PI)-based composites. A series of PI-based composites containing different loading (0–40 wt% or 0–19.6 vol%) of ZWP powder were fabricated by the in-situ polymerization technique. Their structures and properties were characterized by Scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), Impedance meter, Thermal mechanical analysis (TMA) and Thermogravimetric analysis (TGA). The additions of ZWP steadily reduced the TEC of the PI matrix at all loadings studied. A 40 wt% (19.6 vol%) ZWP loading gives a 32.5% (about 15×10^{-6}/K) reduction of TEC. The thermal stability of the ZWP/PI composites can be enhanced with the increment of ZWP powder. The independence of the dielectric constant on frequency is improved by introduction of ZWP particles to PIs. The dielectric loss displays good stability, which indicates that the ZWP/PI composites show potential applications in microelectronic and aerospace industries.

1. Introduction

Aromatic polyimides (PIs) are widely used in many engineering fields as buffer coatings, gas separation membrane, passivation layers, interlayer dielectrics, wafer-scale packages, etc., because of their desirable characteristics such as excellent mechanical properties, good thermal stability, chemical resistance, easy processability and low dielectric constant [1–6]. However, aromatic PIs exhibit relatively higher TEC (about 40–80 $\times 10^{-6}$/K) compared with most ceramics and metals (e.g.: SiO_2: 14 $\times 10^{-6}$/K, Si: 3–5 $\times 10^{-6}$/K, Cu: 16–18 $\times 10^{-6}$/K) [7]. The TEC value is a crucial factor for most structural and functional materials. A relatively higher TEC may cause serious destruction of devices [8], such as

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cracking or delamination. In the case of thin films, TEC is one of the key parameters that represent the degree of a film dimension changed during high temperature process [6]. Although PIs can be used in high temperature circumstances, the high TEC of which limits their use in a variety of advanced applications, such as solar panel used in spacecraft, conformal coatings used in the microelectronics industry and high performance structural materials in aerospace engineering [9,10]. For example, solar panel is composed of several materials including cover glass, silicon rubber, silicon chip and PI, etc. The spacecraft experiences great temperature changes when working in orbit. Under such circumstances, the mismatch of TECs between PI and silicon rubber or silicon chip may lead to the reduction of spacecraft's reliability and service life. So, it is of great significance to improve the thermal expansion coefficient matching of PI with other materials. With the rapid development of electronic industry, the intent to improve the drawback derived from the TEC of PIs arouses more and more attentions.

In the plastics industry, the addition of filler materials to a polymer is a common and effective method to obtain a material with desired thermal properties [11]. To reduce the TEC of PIs, forming hybrid PI composites with inorganic filler materials is a promising approach [1]. In recent years, many researches have been carried out to tune the properties of PIs by incorporating inorganic materials, such as silica particles [1,12], TiO_2 nanoparticles [13], montmorillonite [14], CNT [15], Ti [16] or Al_2O_3 [17], etc. However, the reduction in TEC by these particles is limited because of the positive TEC of the fillers [11].

Compared with most materials that exhibit positive TEC, Zirconium tungsten phosphate ($Zr_2WP_2O_{12}$, denoted as ZWP) displays negative thermal expansion (NTE) of approximately -3 to -5×10^{-6}/K over a broad temperature range from room temperature to 1073 K [18–20]. ZWP comprises ZrO_6 octahedra sharing corners with WO_4 and PO_4 tetrahedra [21] and remains orthorhombic structure down to very low temperatures [18,22]. The NTE behavior of this material results mainly from transverse motions of the bridging O atoms, or the coupled rotation between the octahedral and tetrahedral [23]. Compared with other NET materials reported [24], ZWP is stable under certain pressure and over a large temperature range [25,26]. ZWP also has desirable bending strength and low dielectric constants. When ZWP is used as filler in composites, no phase transition will occur. From an economic perspective, ZWP is a low-cost raw material. Isobe et al. pointed out that ZWP is a novel NTE material [26]. Hence, ZWP should be an excellent and promising candidate for use as an inorganic filler to control the TECs of ceramics, metals, polymers and glasses. However, there are very few reports about ZWP used as filler to tune the TECs of other materials, especially to tune the TECs of PI.

The objective of this presentation is to develop PI-based composites with reduced TEC and also to maintain other favorable bulk properties of the polymer, such as thermal stability and dielectric properties. Thus, ZWP/PI hybrids with different ZWP loading were prepared and the properties of which were investigated.

2. Experimental

2.1. Materials

$ZrOCl_2 \cdot 8H_2O$, $H_{42}N_{10}O_{42}W_{12} \cdot xH_2O$ and $(NH_4)H_2PO_4$ with 99% purity were purchased from ALADDIN REAGENT (Shanghai) co., Ltd. N,N-dimethylformamide (DMF) was purchased from fine chemical engineering research and development Center of GuangDong province, China. Pyromellitic dianhydride (PMDA) and 4, 4′-oxydianiline (ODA) were purchased from Chinese Chemical Reagent Co. Ltd. And other reactants and solvents were used as received if it is not mentioned specifically.

2.2. Sample preparation

Hydrothermal method was used to prepare ZWP powder. $ZrOCl_2 \cdot 8H_2O$, $H_{42}N_{10}O_{42}W_{12} \cdot xH_2O$ and $(NH_4)H_2PO_4$ with the molar ratio of Zr:W:P = 2:1:2 were maintained. During the preparation process, $(NH_4)H_2PO_4$ aqueous solution was added into $H_{42}N_{10}O_{42}W_{12} \cdot xH_2O$ aqueous solution. After reaction, a transparent solution will be formed. And then $ZrOCl_2 \cdot 8H_2O$ was dropwise added into the obtained transparent solution under magnetic stirring and a slurry was formed rapidly. The obtained slurry (ZWP precursor) was then put into a sealed reaction kettle (HZSF12-type, made by GONG YI INSTRUMENT AND EQUIPMENT CO., LTD., Henan province, China.). After reacting for 48 h at 130 °C, the reaction mixture was then taken out and cleaned in a centrifuge for 5 times to obtain the precipitates. The precipitates were filtrated and dried at 80 °C in a vacuum drying oven, followed by annealing in a muffle furnace at 900 °C for 4 h to get white ZWP powder. Usually, hydrothermal methods can yield nanoparticles. However, the ZWP powder we prepared was a little rough. So, the obtained powder was then ball mixed in a planetary muller for 10 h to refine the particles. Furthermore, thinner particles may improve the composite effects [27]. After fully ball milling, the powder was pressed by cold pressing to form Φ10 mm × 4 mm cylinders. The obtained cylinders were sintered at 900 °C for 4 h and cooled along with the furnace for thermal expansion coefficient test [28].

ZWP/PI hybrid composites containing different loading ZWP powder were fabricated by in-situ polymerization technique. A 1 g of the vacuum dried diamine monomer (ODA) was added into 20 mL DMF. The mixture was stirred thoroughly at room temperature to obtain a clear solution. Different contents (0 wt%, 5 wt %, 20 wt %, 30 wt %, 40 wt % or 0 vol%, 1.9 vol%, 8.4 vol%, 13.6 vol%, 19.6 vol%) of ZWP powder were then added into this solution and allowed to mix by stirring until the solution became white. A 1.145 g of the vacuum dried dianhydride monomer (PMDA) was added gradually during 40–60 min. And at the same time, the combined reaction mixture was stirred at room temperature for 4–5 h by a magnetic stirrer. A mixed solution of PAA/ZWP/DMF (PAA is the abbreviation of polyamic acid, the precursor of PI) with pale-yellow color was obtained. The mixed solution was dried at 80 °C for 24 h, followed by heat-treating for 1 h at 120 and 180 °C, and then at 250 and 300 °C for 4 h with temperature increasing rate of 5 °C/min [8]. After the above mentioned heat treatment, a complete imidization of PAA to PI would be obtained. The as-prepared ZWP/PI blended powder was grinded and pressed into cylinders of Φ10 mm × 4 mm for the following characteristic measurements.

2.3. Instrumentation and measurements

X-ray diffraction (XRD) analysis of the as-prepared ZWP powder was carried out with the BRUKER D8 Advance Diffractometer (German) using a Cu K_α X-ray source ($\lambda = 0.15406$ nm) operating at 40 KV and 740 mA, scanning at a rate of 2°/min in the 2θ range from 10 to 33°. Scanning electron microscopic (SEM) micrographs were obtained on a JSM-6700F/INCA-ENERGY (Japan) SEM. Energy dispersive X-ray analysis (EDX) studies were recorded on a field emission scanning electron microscope (Nova 400 nanoSEM, FEI Company, USA) equipped with an energy dispersive X-ray spectroscope (INCA IE 350 PentaFET X-3,Oxford, UK). The particle size of the as-prepared ZWP powder was measured through SEM image by Nano Measurer 1.2 program [29] and confirmed by Zetasizer Nano ZS90 (MALVERN, England). Thermal mechanical analysis (TMA) of the as-prepared ZWP cylinder and ZWP/PI composites were obtained on a LINSEIS-L76 (German). The relative densities of the as-prepared ZWP ceramic and ZWP/PI composites were calculated by using Archimedes technique. The ZWP/PI composites were