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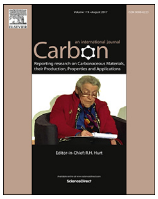

Largely improved dimensional stability of short carbon fiber reinforced polyethersulfone composites by graphene oxide coating at a low content

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ABSTRACT

For aviation and automobile applications, etc., high dimensional stability is critically important since the mismatch in linear coefficient of thermal expansion (LCTE) between polyethersulfone (PES) and metal materials would lead to dimensional instability. In this work, the GO-coating treatment is proposed to greatly enhance the dimensional stability of injection molded short carbon fiber (SCF)/PES composites. It is shown that the LCTE of the GO-coated SCF/PES composites is significantly reduced along both the longitudinal and transverse directions. At the low content of 0.5 wt% GO, the LCTE of the GO-coated SCF/PES composite is largely reduced by 67.0% along the longitudinal direction and 28.9% along the transverse direction in the temperature range from -196 °C to 150 °C. The enhanced dimensional stability by the addition of GO-coated SCFs is much higher than that by the addition of un-treated SCFs or the separate addition of GO and SCFs. The dynamic mechanical analysis (DMA) shows that the composite storage modulus and loss modulus are effectively enhanced by the GO-coating, indicating that the GO coating treatment brings about a strong interfacial interaction between SCFs and PES. It is regarded that the chain movement of PES would be restricted by the enhanced SCF/PES interfacial interaction and the restricted movement of PES chains by the strong SCF/PES interfacial adhesion finally leads to a significantly lowered composite LCTE.

1. Introduction

Polyethersulfone (PES) as a high performance special engineering thermoplastic possesses excellent thermal oxidation and chemical resistance, relatively high modulus, mechanical strength and heat deflection temperature [1]. In recent years, PES has attracted intensive attentions as preferred replacements of metal materials or to match its usage with metal materials in aviation, automobile, microelectronics, and membrane separation, etc. [2]. However, its relatively high linear coefficient of thermal expansion (LCTE) compared to metal materials has limited these applications and the mismatch in the LCTE between PES and metal materials in combination systems could lead to dimensional instability and deterioration of lifetimes and even destroy the integral structure of the devices due to the development of residual thermal stresses as the temperature changes [3]. Hence great efforts have been devoted to the development of low LCTE polymer composites. For instance, carbon fibers (CFs), glass fibers (GFs) and GO etc. are introduced into polymer matrices to make composites with enhanced mechanical properties and reduced LCTE [2,4]. Especially, CFs are widely used as reinforcements in polymer-matrix composites owing to their excellent mechanical property, high thermal and electrical conductivity, resistance to corrosive environment, and low density [5]. As reinforcement with negative thermal expansion property, namely shrinking on heating and expanding on cooling, the addition of CFs can not only enhance the mechanical properties but also reduce the LCTE and hence improve the dimensional stability for polymer matrices [6]. In particular, the LCTE of CF/polymer composites in the direction of the CF alignment can be effectively decreased [7]. The reduction in the LCTE of polymer matrices by introduction of the CFs results from several aspects [8]: some

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amounts of polymer matrices are substituted by CFs; the mobility of polymer chain is restricted due to the strong interaction at the CF/polymer interface; physical confinement of the polymer occurs when anisotropic CFs are mixed with polymer matrix. However, the effectiveness for the LCTE reduction of polymer by fibers critically depends on the fiber-matrix interfacial interaction since good interfacial bonding can cause a strong mechanical restriction on polymer molecular chain deformation as temperature varies [9].

In recent years, various CF surface modification methods such as electrochemical treatment, plasma etching, high energy irradiation, grafting and sizing treatment, etc. have been applied to increase the interfacial adhesion between CFs and polymer matrix [10]. As for the sizing treatment, it can also protect CFs from mechanical damage during the processing and improve the wetting of CFs by the polymer matrix. GO as the graphene derivative and a potential multifunctional sizing agent can be uniformly dispersed and firmly adsorbed on the surfaces of CFs to synthesize a new hierarchical reinforcement due to its unique two-dimensional structure, large specific surface area, etc. Meanwhile, it contains various oxygen functional groups such as epoxide, hydroxyl and carbonyl groups [11]. Therefore, it is expected that the GO coating would enhance the CF/PES interfacial interaction [12] and thus the chain movement of polymers may be effectively restricted by coated CFs. In addition, GO belongs to a negative thermal expansion material [13], it can also be used to reduce the LCTE of polymer composites.

Recently, the LCTE reduction of polymers by introducing micro-sized or nano-sized fillers has attracted interests. Suzuki et al. [14] fabricated mesoporous silica/epoxy polymer composites through a solvent evaporation process. The result revealed that the LCTE gradually decreased as the amount of the doped mesoporous silica increased and mesoporous silica particles showed a great effect in lowering the LCTE. Badrinarayanan et al. [6] fabricated unidirectional CF reinforced multiscale composite laminates based on the bisphenol E cyanate ester (BECy)/ZrW_2O_8 nanocomposite matrix. The results revealed that incorporation of nanoparticles facilitated a reduction in LCTE of the composites. Huang et al. [15] studied the combined effect of talc particles and glass fibers (GFs) on thermal expansion performance of the filled high density polyethylene (HDPE) composites. The result displayed that the use of silane-modified GFs had a much larger effect in reducing the LCTE of filled composites, compared with the use of un-modified talc particles due to enhanced GF bonding to the matrix, larger aspect ratio and GF alignment. Shokrieh et al. [16] incorporated carbon nanofibers (CNFs) into an epoxy matrix to make composites and then studied the effect of CNFs on the LCTE of composite. The result showed that the LCTE of the epoxy matrix was reduced by adding small amounts of CNFs. Wu et al. [17] reported the effect of basalt fiber (BF) on the LCTE of HDPE. It was shown that the BF/HDPE composites exhibited the reduced LCTE to some degree compared to the neat HDPE. Wu et al. [18] incorporated graphene nanoplatelets (GNPs) into polyetherimide to reduce the LCTE of the injection molded samples. It was found that the GNP particles were very effective in terms of reducing the LCTE. Fasanella et al. [19] computed the thermomechanical properties of cured epoxy resins reinforced with pristine and covalently functionalized carbon nanotubes by the molecular dynamics simulation. The decrease in thermal expansion was expected along the direction of the nanotubes for the nanocomposites compared to the neat epoxy. Liu et al. [20] fabricated a complex reinforced polyimide composite interposer comprised with conductive Ni cylinders, ordered Ni grid and SiC nano-whiskers. Compared with the traditional design, the LCTE of the complex reinforced composite interposer was decreased by 10.1%. On et al. [21] studied the effect of microwave treatment on the LCTE of meta-aramid nanofiber mats reinforced epoxy composites. As a result, the post-treated meta-aramid nanofiber mats exhibited an effectively reduced LCTE. Lin et al. [22] used acrylamide-modified reduced graphene oxide (AA-RGO) and thiophenol modified silver nanowires (mAgNWs) to reinforce silicone rubber (SR). The result showed that the LCTE of the mAgNW/AA-RGO/SR nanocomposites was 148.3 ppm/°C, which was considerably lower than the LCTE of the neat SR, 310.0 ppm/°C.

When a body undergoes a temperature change, there will be a change in its dimensions relative to its original dimensions. The LCTE is defined as the change in the linear dimension of the body per unit change of temperature. For a short fiber reinforced polymer composite, the mathematical formulation of the micromechanical models of linear coefficient (α_c^L and α_c^T) of thermal expansion along the longitudinal and transverse directions to fibers are given as follows [23,24]:

$$\alpha_c^L = \frac{\alpha_f^L E_f V_f + \alpha_m E_m \left(1 - V_f\right)}{E_f V_f + E_m \left(1 - V_f\right)} \tag{1}$$

$$\alpha_c^T = \left(1 + \upsilon_f\right)\alpha_f^L V_f + (1 + \upsilon_m)\alpha_m \left(1 - V_f\right) - \alpha_c^L \upsilon_C \tag{2}$$

where α_f^L and α_m are the LCTE of the fiber and the matrix, respectively. υ_f, υ_m and υ_C are the Poisson's ratio of the fiber, matrix and composite, respectively. E_m and E_f are the tensile modulus of the fiber and matrix, respectively. V_f is the fiber volume fraction. Nonetheless, the micromechanical model does not consider the influence of interfacial interaction between fibers and polymer matrix. Actually the interfacial property would have an effect on the composite thermal expansion since a better interfacial bonding can lead to a stronger physical confinement [25] and thus lower the composite LCTE.

The injection molding technique has the advantages of fast processing, low cost and easy operation, etc [24]. In this work, the effect of GO coating on the LCTE of injection molded SCF/PES composites is investigated. The GO coating is proposed to significantly enhance the SCF/PES interfacial adhesion due to the hydrophilic oxygen-functional groups in GO basal plane [11,26]. The results of the dynamic mechanical analyzer (DMA) and the scanning electron microscope (SEM) of the tensile failure surfaces prove the strong interfacial interaction between the coated SCFs and the PES. The LCTE shows a large reduction by the GO coating. Meanwhile, for the purpose of comparison, the GO/SCF/PES composites via separate addition of GO and SCFs are obtained. The results indicate that the GO-coated SCF/PES composites display the relatively significantly lower LCTE particularly in the longitudinal direction than that for the GO/SCF/PES composites via separate addition of GO and SCFs. Consequently, it is clear that the GO coating has a significant role in reducing LCTE and thus enhancing the dimensional stability of SCF reinforced PES composites.

2. Experimental

2.1. Materials

Polyethersulfone (PES, granules, E3010) and short carbon fibers (SCFs, 6 mm length, C30 S003/6 APS) were respectively obtained from BASF and SIGRAFIL, Germany. Other starting solvents and materials were obtained from commercial vendors, and were used without further purification.

2.2. Preparation of GO and PES composites

Graphite powders were oxidized through the acid oxides consisting of concentrated sulfuric acid, potassium permanganate and sodium nitrate via the modified Hummers method [27] and graphite