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Titanate nanotubes and nanosheets as a mechanical reinforcement of water-soluble polyamic acid: Experimental and theoretical studies

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ABSTRACT

Titanate nanosheets (TiNS), titanate nanotubes (TiNT), and scrolled titanate nanosheets (STiNS) were used to synthesise polymer nanocomposites by solution processing. The hardness was found to increase by 90% on addition of 2% TiNS while the modulus (*Er*) increased by 103% compared to the pure polymer. Small angle X-ray scattering (SAXS) measurements of composite films were used to study alignment of nanostructures within the polymer. The obtained data on mechanical properties of composites have been tested against theoretical values and it was established that both nanostructures alignment as well as their mechanical properties affect the hardness and modulus of the polymer composites. At a low content of TiNS, the reinforcement behaviour matched well with Halpin-Tsai theory which assumes the filler has unidirectional orientation. After addition of 2 wt% TiNT, the hardness and modulus of the polyamic acid salt composites increased by 91% and 165%, respectively, and were higher than theoretical predictions, indicating that both TiNT and STiNS, prepared by hydrothermal synthesis, may have higher mechanical properties than bulk TiO_2. At a high filler loading (>2 wt%), the mechanical properties of composites do not fit established theories due to agglomeration of titanate nanostructures.

1. Introduction

Polymer nanocomposite materials consist of a hybrid organic matrix containing dispersed nanostructure filler. The structures are widely varied from zero (sphere, cubes, and polyhedrons), one (rods, fibres, tubes), two (sheets, discs, plates) dimensional, and complex shapes (flower, leaf, etc.) These nanofillers provide significant improvement in the polymer properties at low filler loadings due to the large degree of contact between nanofiller and polymer. For example, the small addition of exfoliated clay (4.7 wt %) can increase the flexural modulus of nylon-6 by four times at 120 °C [1]. Successful application of clay filler to improve the mechanical properties of polymers requires further research on other nanostructure based polymer nanocomposites containing, e.g., metal oxides, hydroxides, nitrides, and chalcogenides. In the past decades, titanium oxide with various structures (e.g., nanotubes and nanosheets) has been studied. Titanium oxide single layer nanosheets (TiNS), the graphene analogue, have been discovered by Sasaki, *et.al.* [2] in the mid-1990s. These nanosheets can be obtained by a three-step process involving solid-state reaction, acid ion-exchange, and exfoliation [2]. The resulting product is a highly crystalline single layer sheet possessing unique properties which differ from bulk titanium oxide [3]. These nanosheets have been applied in various functional nanocomposite polymers, for example acting as photo-initiators for water-soluble vinyl monomers polymerization owing to the photocatalytic properties of titanate nanosheets [4]. Proton-donating monomers such as *N*-isopropylacrylamide (IPAAm), acrylamide (AAm), and acrylic acid (AAc) may produce strong bonds to the negatively charged titanate nanosheets and polymerize with TiNS as a physical photo-crosslinker. The polymerization occurs near the TiNS and the polymer is trapped by adjacent TiNS producing a highly sensitive optical response to thermal stimuli. The proton conductivity of sulfonated poly(ether ether ketone) (SPEEK) membranes is enhanced by up to two times by low loading of titanate nanosheets (1.67 wt%) [5]. Such materials are stable at high temperatures (140 °C) and in a wet environment (100% relative humidity). Adding TiNS to polyethylene naphthalate (PEN) films significantly decreases helium gas permeability [6]. However, there is no systematic study on the mechanical reinforcement effects of titanate nanosheets on polymer nanocomposite.

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In contrast to titanate nanosheets, titanate nanotubes (TiNT) only require a one-step alkaline hydrothermal treatment. Alkali treatment at high temperature (*ca.* 110 °C) induces scrolling of the titanate nanosheets producing titanate nanotubes [7]. This kind of nanotubes was discovered in 1997 by Kasuga, *et.al.* [8]. Incorporation of elongated titanates into the polymers can improve the transport properties in nanofiltration membranes [9], gas sorption capacity [10], corrosion resistance [11], and thermal properties [12]. It has also been used to strengthen polymer blends such as polyethylene oxide and chitosan [13]. At 25 wt% loading of titanate nanotubes, the polymer blend was found to be approximately 2.6 times harder compared to the neat polymer blend and 3.4 times stiffer. Considering this promising enhancement of nanofiller at low loadings, the reinforcement effect needs to be further studied. Instead of nanotubes, the alkaline hydrothermal method can also produce nanosheets with scrolled morphology at lower processing temperatures [7]. The study of these scrolled nanosheets (STiNS) is still very limited. Titanate nanotubes and scrolled nanosheets due to the simplicity of their manufacturing and abundance of the precursors, can be useful low cost alternative to carbon nanostructures such as graphene and carbon nanotubes for certain applications (e.g., structural, thermal protection, gas and UV barrier).

In this work, titanate nanotubes (TiNT), scrolled titanate nanosheets (STiNS), and titanate nanosheets (TiNS) have been used to enhance the mechanical properties of water soluble polyimide precursors, namely, polyamic acid salt (PAAS). Titanate nanotubes and nanosheets possess high surface charges making them easily dispersed and stabilised in aqueous solvent, hence the choice of water-soluble polymers. Moreover, the polyamic acid salt is a more stable form of polyamic acid which is the polyimide precursor [14]. The morphology of the titanate nanosheets and nanotubes were examined with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Nanoindentation has been used to study the reduced modulus (*Er*) and hardness (*H*) of the composites. Experimental results are compared with theoretical models, such as those due to the modified rule of mixtures [15], Halpin-Tsai [16], and Halpin-Kardos [17], to study and evaluate the existing models. The dispersion of titanate nanosheets and nanotubes in polyamic acid is studied by TEM to determine its correlation with mechanical properties and compared to that of the titanate nanostructures-polyamic acid salt composite. Small-angle x-ray scattering (SAXS) was used to determine the interlayer spacing of nanosheets inside the polymer, to confirm incorporation of nanotubes within the polymer and investigate the degree and alignment of nanostructures.

2. Theoretical background and experimental

It is important to study the experimental data alongside existing theoretical models. Clay [18], graphene [19], and carbon nanotubes [20] are often used to evaluate micromechanical models for nanocomposite reinforcement. Herein, we report titanate nanotubes, scrolled titanate nanosheets, and titanate nanosheets as a mechanical reinforcement of water-soluble polyamic acid.

2.1. Theoretical background

The theoretical models used in this particular research are models able to predict composites containing matrix and filler as reinforcements with the basic assumptions of a void free matrix and no residual stress in composites (stress-free state). Modified rule of mixtures, Halpin-Tsai, and Halpin-Kardos were chosen for this purpose.

2.1.1. Modified rule of mixtures

The rule of mixtures is a well-known model based on the Voigt equation [21] that is used to predict continuous unidirectional fibre composites. This model is also known as the iso-strain model which assumes the filler and matrix have the same elongation when a certain load is applied to the composite. However, it is not suitable for evaluating mechanical properties of some composites as it often overestimates the properties [22,23]. Hence, the modified rule of mixtures, which is a semi-empirical model, is applied [15]. The modified rule of mixtures is:

$$E_c = \chi_f E_f V_f + E_m (1 - V_m) \tag{1}$$

where E_c, E_f, and E_m are the moduli of composite, filler, and matrix, respectively. χ_f is a particle strengthening factor with values between 0 and 1. V_f and V_m are the volume fractions of filler and matrix obtained by converting the weight filler fractions, assuming the densities of TiO_2 (4.23 g ml^{-1}) and polyamic acid (1.04 g ml^{-1}). This equation can also be applied to estimate the hardness of the composite by substituting the modulus for hardness. The modulus and hardness of the filler is taken from CRC Materials Science and Engineering Handbook [24], which are 282.76 GPa and 10.99 GPa, respectively, considering TiNS, STiNS, and TiNT structures as TiO_2. The Young's modulus and hardness of the matrix are adapted from nanoindentation of the polyamic acid salt.

2.1.2. Halpin-Tsai equation

The Halpin-Tsai equation is a model to estimate reinforcement of unidirectional oriented short fibres and has successfully predicted the reinforcement of carbon nanotubes at low filler content (>1 wt%) [25]. It can also be adapted to predict the modulus of polymer nanocomposites with nanosheets (e.g., clay [18] and graphene [26]) as filler. The Halpin-Tsai equation is:

$$\frac{E_c}{E_m} = \frac{1 + 2A_f \mu \phi_f}{1 - \mu \phi_f} \tag{2}$$

where E_c and E_m are the moduli of the composite and matrix (PAAS), respectively. The Young's modulus of the matrix (PAAS) is adapted from nanoindentation measurements of pure PAAS. A_f is the filler aspect ratio (l/h), in this case (l) is the nanosheets or nanotubes length and (h) is the nanosheets thickness or nanotubes diameter. Φ_f is the volume fraction of filler. μ is a geometric factor, given by:

$$\mu = \frac{\left(E_f / E_m\right) - 1}{\left(E_f / E_m\right) + 2A_f} \tag{3}$$

where E_f is the modulus of TiO_2 taken from literature [24]. The Halpin-Tsai equation is also able to predict the hardness of micro and nanocomposites by simply exchanging the modulus with hardness [27]. The hardness of the matrix (H_m) is determined by nanoindentation of pure PAAS while the hardness of TiO_2 (10.99 GPa) is taken from the literature [24].

2.1.3. Halpin-Kardos equation

Originally, the Halpin-Kardos equation was applied to randomly oriented short fibres with a quasi-isotropic laminate assumption involving the $[0/+45/90/-45]_n$ configuration [17]. However, the expression can also be adapted. It has been successfully used to predict the reinforcement of nanosheets (e.g., clay) up to 2 wt% in a polymer blend [18]. The authors argued that the tactoid phase of clay may act in a similar fashion to short fibres. The Halpin-Kardos equation is: