

Incorporation of titanate nanosheets to enhance mechanical properties of water-soluble polyamic acid

Christian Harito, Dmitry V Bavykin, Frank C Walsh

Faculty of Engineering & the Environment, University of Southampton, Southampton, United Kingdom, SO17 1BJ

E-mail : ch8g13@soton.ac.uk

Abstract. Pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA) were used as monomers of polyimide. To synthesise a water soluble polyimide precursor (polyamic acid salt), triethylamine (TEA) was added to polyamic acid with a TEA/COOH mole ratio of 1:1. Titanate nanosheets were synthesised by solid-state reaction, ion-exchanged with acid, and exfoliated by TEA. Exfoliated titanate nanosheets were mixed with water soluble polyamic acid salt as reinforcing filler. Drop casting was deployed to synthesise polyamic acid/titanate nanosheet nanocomposite films. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to study the morphology and dispersion of nanosheets in the colloidal dispersion and the solid film composite. Modulus and hardness of nanocomposites was provided by nanoindentation. Hardness increased by 90% with addition of 2% TiNS while modulus increased by 103% compared to pure polymer. This behaviour agrees well with Halpin-Tsai theoretical predictions up to 2 wt% filler loading; agglomeration occurs at higher concentrations.

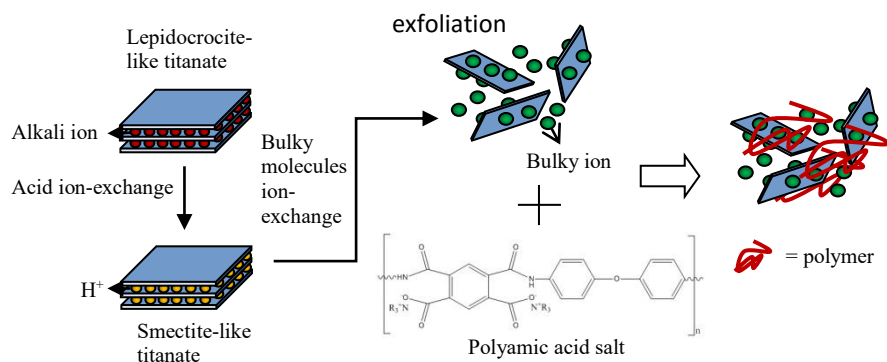


Figure. Illustration of titanate nanosheets exfoliation and incorporation in polyamic acid salt

1. Introduction

Polymer nanocomposites consist of a hybrid organic matrix containing a dispersed nanostructured filler. The filler can provide a significant improvement in polymer properties at low filler loading, due to the high degree of contact between filler and polymer. For example, small addition of exfoliated clay (4.7 wt%) can increase flexural modulus of nylon 6 by four times at 120°C [1]. Successful application of a clay filler to improve the mechanical properties of polymer requires further research on other nanosheet based polymer nanocomposites containing, e.g., graphene [2], boron nitride nanosheet [3]. Despite their increasing importance, there are few recent studies of recently titanate nanosheets for the reinforcement of polymer nanocomposites [4].



Titanate nanosheets (TiNS) are single sheet inorganic materials created by exfoliation of lepidocrocite-like titanium oxide. Due to their unique properties, this so-called graphene analogue attracts international research interest. It has been applied in some polymer nanocomposites for functional purposes. Titanate nanosheets act as a photo-initiator for water-soluble vinyl monomers owing to the photocatalytic properties of titanate nanosheets [5]. Proton-donating monomers such as N-isopropylacrylamide (IPAAm), acrylamide (AAM), and acrylic acid (AAc) can strongly bond to the negatively charged titanate nanosheets and polymerize with TiNS as a physical photo-crosslinker. The polymerization occurs near the TiNS and is trapped by adjacent TiNS, producing a highly sensitive optical response to thermal-stimuli. The proton conductivity of sulfonated poly(ether ether ketone) (SPEEK) membrane can be doubled by a low loading of titanate nanosheets (1.67 wt%) [6] and the composite is stable at high temperature (140 °C) and in a wet environment (100% relative humidity). Adding TiNS to polyethylene naphthalate (PEN) film significantly decrease helium gas permeability [7]. However, systematic study about mechanical reinforcement effects of titanate nanosheets on the polymer nanocomposite is still limited [8].

In this work, titanate nanosheets (TiNS) have been used to enhance the mechanical properties of polyamic acid salt (PAAS). The morphology of titanate nanosheets is imaged by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Nanoindentation has been used to examine the reduced modulus (E_r) and hardness (H) of the composites. Experimental results are compared with theoretical models due to Halpin-Tsai [9] and Halpin-Kardos [10]. The dispersion of titanate nanosheets in polyamic acid is studied by TEM to determine its effect on the mechanical properties of resultant titanate nanosheets-polyamic acid salt composites.

2. Experimental Methods

Synthesis method of titanate nanosheets, polyamic acid salt, and composites are considered.

2.1. Synthesis of titanate nanosheets

A synthesis method for single-layer titanate nanosheets adapted from Sasaki *et.al.* [11] Sasaki's single-layer titanate nanosheets are based on two starting materials as alkali precursors (K, Li, Rb, Cs) and TiO₂ powder. For synthesis of titanate nanosheets by the caesium route, TiO₂ (Degussa P25) from Aeroxide and Cs₂CO₃ from Sigma-Aldrich were used without further purification. There are three steps to synthesis single-layer titanate nanosheets. Firstly, solid-state reaction of TiO₂ and Cs₂CO₃ was conducted based on the work of Grey *et.al.* [12] 2.6 g of Cs₂CO₃ and 2 g of TiO₂ (molar ratio 1: 5.3) was mixed, ground and put in a platinum crucible, an inert crucible being crucial to prevent reaction of alkali precursor and crucible, for one hour heating at 800 °C. The mixture was allowed to cool

spontaneously. It was ground then heated at 800 °C for 20 h. The material was ground then the heat treatment cycle was repeated. The resulting product was a white powder of lepidocrocite-like caesium titanate ($\text{Cs}_{0.7}\text{Ti}_{1.825}\text{Y}_{0.175}\text{O}_4$) with Y representing a vacancy [13,14].

Secondly, acid ion-exchange was used to create smectite-like acid titanate ($\text{H}_{0.7}\text{Ti}_{1.825}\text{Y}_{0.175}\text{O}_4 \cdot \text{H}_2\text{O}$) [13,14]. 2.4 g of $\text{Cs}_{0.7}\text{Ti}_{1.825}\text{Y}_{0.175}\text{O}_4$ was stirred with 96 mL of 1 M HCl for 4 days. The acid solution was replaced with a fresh acid solution every day to maintain the amount of H^+ ions for acid leaching of Cs^+ ions. Then, the solution was decanted with deionized (DI) water three times followed by vacuum filtration using 0.2 μm nylon membrane and washed with distilled water until the conductivity around 10 $\mu\text{S cm}^{-1}$.

Thirdly, bulky molecules ion-exchange was demonstrated by exfoliating 0.08 g of $\text{H}_{0.7}\text{Ti}_{1.825}\text{Y}_{0.175}\text{O}_4 \cdot \text{H}_2\text{O}$ with 20 mL of distilled water and 400 μL triethylamine (TEA) with bath ultrasonicator for 9 h. The solution was kept for 4 days to separate non-exfoliated sheets at the bottom. Finally, the upper, exfoliated nanosheets were directly used to make composites.

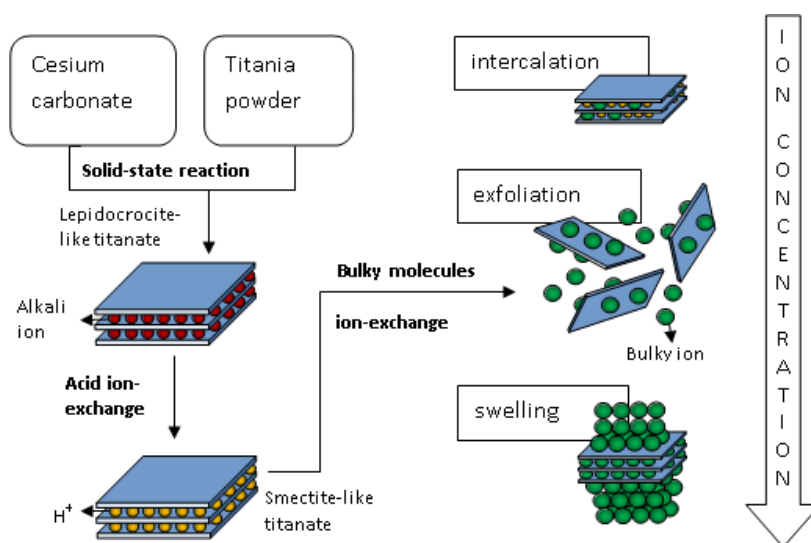


Figure 1. Schematic representation of titanate nanosheet synthesis

2.2. Synthesis of polyamic acid salt

The work of Lee, *et.al.* [15] has been used as a guide to synthesise polyamic acid salt. An aromatic polyamic acid salt were prepared from pyromelliticdianhydride (PMDA) and 4,4'-oxydianiline (ODA) as monomers and N,N-dimethylacetamide (DMAc) as a solvent. All the reactions were shielded by nitrogen gas. As a typical example, a mixture of 1.201 g of ODA

(1 mol) and 22.59 g of DMAc was stirred in a 250 mL round bottom flask at room temperature (22 °C). After ODA had dissolved, 1.309 g of PMDA (1 mol) was added to the solution followed by stirring for 1 day, yielding a 10 wt% DMAc solution of polyamic acid. 1.656 mL of triethylamine (TEA; 2 mol of monomer) was added. Local white precipitation was visible upon addition of TEA to the solution as stated by Kreuz, *et.al.* [16] and disappeared after approximately 30 min. The resulting solution was poured into acetone and filtered with a 0.2 µm pore size nylon membrane, followed by washing twice with acetone. After drying at 22 °C for 24 h, light yellow PAAS powder was collected and stored at 22 °C and 40±5% relative humidity.

2.3. Synthesis of polyamic acid salt-titanate nanosheet composites

All composites in this work were made by solution mixing. A known concentration (determined by UV-vis spectrometry) of titanate nanosheet colloidal suspension was mixed with PAAS powder to produce 5 wt% of PAAS-TiNS aqueous solution with various concentration of TiNS (0.5, 1, 2, 3, and 5 wt% of solid). For pure polymer, 0.215 g of PAAS was stirred in 4 mL distilled water and 80 µL TEA to assist dissolution of PAAS, yielding 5 wt% of PAAS aqueous solution. The solutions were stirred for 3 days and drop cast on glass. The drop cast solutions were kept at 22±2 °C and 40±5% relative humidity for 4 days to dry and achieve an equilibrium moisture content in the films.

2.4. Characterisation

The morphology of titanate nanosheets was examined by transmission electron microscopy (TEM) (JEOL-3010) and field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6500). To prepare TEM samples, a diluted colloidal suspension was dropped on a copper grid containing perforated carbon film and dried for 1 day in 22 °C. A diluted colloidal suspension of titanate nanosheets was dropped on top of a silicon wafer for SEM characterisation. The concentration of titanate nanosheet suspension was determined with UV-vis spectroscopy. TEM (JEOL-3010) was employed to study dispersion of titanate nanosheets in polyamic acid salt. Samples were dropped on a copper grid with perforated carbon film and spin coated at 4300 rpm for 1 min to achieve a very thin film for TEM. The optical properties of polymer composites were evaluated with a 20.1 megapixel camera.

The reduced modulus and hardness were obtained with a nanoindenter (Nanotest Platform 3, Micro Materials Ltd, UK). Reduced moduli were converted to Young's moduli using the Oliver-Pharr equation [17]. To prepare the samples, a sliver of the film (around 0.5 cm x 0.5 cm) was glued by epoxy glue to the soda-lime glass with the smoother surface (cast side) on top to be measured. Then,

the glass was glued with acrylic glue to cylinder holder. The cylinder holder with glass and samples on top was put inside the nanoindenter to be measured. A Berkovich (3-side pyramidal) diamond tip was employed for nanoindentation. A constant loading and unloading rate of 20 mN s^{-1} were applied with 30 seconds holding time after reaching the maximum depth. 20 indentations were performed on each sample at a 0.5 mN applied load.

3. Results and Discussion

3.1. Morphology of titanate nanosheets

The structure of the nanosheets is shown in Figure 2.

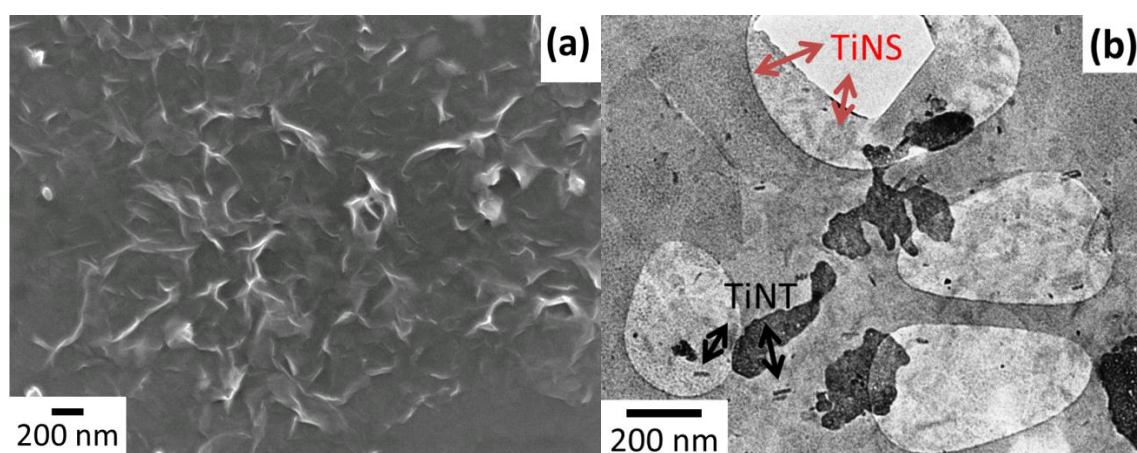


Figure 2. Morphology of titanate nanosheets: (a) SEM Images; (b) TEM Images

Here we report the use of triethylamine to exfoliate titanate nanosheets. The morphology of titanate nanosheets is shown in Figure 2a. The nanosheets tend to restack into a large platelet when dried, creating a tactoid phase or ‘skewed’ agglomerates [18]. TEM is needed to identify the size of the nanosheets. TEM images of TiNS can be seen in Figure 2b. The extremely thin nanosheets result in a very faint contrast, making it hard to distinguish nanostructured material from the background substrate¹⁹. Instead of single layers, some nanosheets stack horizontally on the substrate and become more prominent than single layer nanosheets. The colloidal suspension consists mainly of small, irregularly shaped nanosheet particles with a diameter of *ca.* 100 nm. However, there are some large sheets with a diameter of *ca.* 300 nm together with very small nanotubes (*ca.* 50 nm in length). According to our previous work [20] titanate nanosheets tend to scroll into nanotubes in an alkaline environment. Such scrolling may also occur with very small nanosheets in triethylamine solution.

3.2. Experimental and theoretical analysis of the mechanical properties of polyamic acid salt-titanate nanosheet composites

Nano indentation and transmission electron microscopy were used to study the behaviour of titanate nanosheets embedded in polymer at controlled concentrations (0.5, 1, 2, 3, 5 wt%). TEM images of PAAS/TiNS are provided in Figure 3. At low concentration (1 wt%, Figure 3a), titanate nanosheets tend to retain their exfoliated form inside the polyamic acid salt. Very thin and small nanosheets (*ca.* 100 nm long) were mostly well dispersed, with some traces of few layer nanosheets. This shows that the polymer may interact well with the titanate nanosheets preventing agglomeration. However, some nanosheets lay down on the substrate in a very thin layer which were difficult to observe. At 3 wt% of titanate nanosheets, the distance between adjacent nanosheets became closer and van der Waal's forces between nanosheets became predominant, resulting in agglomerates (Figure 3b). Such agglomerates are likely to form elongated, 'skewed' assemblies of densely packed nanosheets.

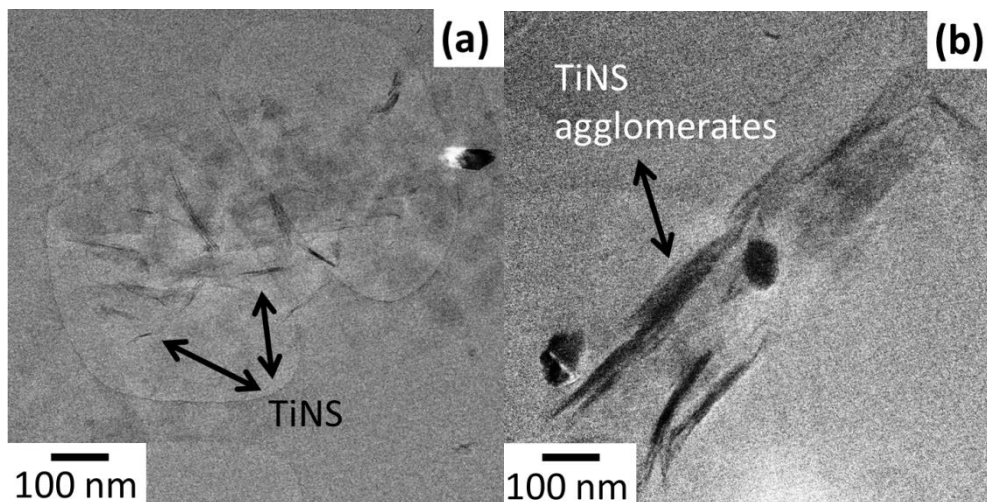


Figure 3. TEM images of titanate nanosheets incorporated into the polyamic acid salt matrix at (A) 1 wt% and (B) 3 wt% of TiNS.

To study and analyse the reinforcement effect of titanate nanosheets, nanoindentation data of the polyamic acid salt-titanate nanosheet (PAAS/TiNS) were compared with theoretical predictions due to Halpin-Tsai [9] and Halpin-Kardos [10]. Halpin-Tsai is a well-known model to estimate reinforcement of unidirectional oriented short fibres and has been successfully used to predict the reinforcement of carbon nanotubes at low filler content (>1 wt%) [21]. It can also be adapted to predict the modulus of polymer nanocomposite with nanosheets (e.g., clay and graphene) as filler [22,23]. The modified Halpin-Tsai equation is:

$$\frac{E_c}{E_m} = \frac{1 + 2A_f \mu \phi_f}{1 - \mu \phi_f} \quad (1)$$

Where E_c and E_m are the Young's modulus of composite (PAAS/TiNS) and matrix (PAAS), respectively. The Young's modulus of matrix (PAAS) is adapted from nanoindentation measurements of pure PAAS. A_f is the filler aspect ratio (l/h), which in this case (l) is the nanosheet length (100 nm) and (h) is the nanosheet thickness (0.75 nm, assuming all the nanosheets are completely exfoliated to single layers). Φ_f is the volume fraction of filler which obtained by converting the weight filler fraction, knowing the density of TiO_2 (4.23 g mL⁻¹) and polyamic acid (1.04 g mL⁻¹). μ is a geometric factor, which is

$$\mu = \frac{E_f/E_m - 1}{E_f/E_m + 2A_f} \quad (2)$$

Where E_f is modulus of TiO_2 (282.76 GPa, by assuming TiNS as TiO_2) as taken from the CRC [24]. The Halpin-Tsai equation is also able to predict hardness of micro and nanocomposite by simply changing the modulus with hardness [25]. 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 literature [24].

The Halpin-Kardos equation can also be used for comparison. Originally, this equation was applied to randomly oriented short fibres with a quasi-isotropic laminate assumption involving the $[0/+45/90/-45]_n$ configuration [10]. However, the expression can be modified and has been successfully used to predict the reinforcement of clay up to 2 wt% in a polymer blend [23]. The authors argued that the tactoid phase of clay may act in a similar fashion to short fibres. The modified Halpin-Kardos equation is:

$$\frac{E_c}{E_m} = \frac{3}{8} \left[\frac{1 + 2A_f \eta_L \phi_f}{1 - \eta_L \phi_f} \right] + \frac{5}{8} \left[\frac{1 + 2\eta_T \phi_f}{1 - \eta_T \phi_f} \right] \quad (3)$$

Where η_L and η_T can be determined with the following equations

$$\eta_L = \frac{E_f/E_m - 1}{E_f/E_m + 2A_f} \quad (4)$$

$$\eta_T = \frac{E_f/E_m - 1}{E_f/E_m + 2} \quad (5)$$

To obtain the hardness, this equation was modified by substituting modulus for hardness. Hardness and modulus of polyamic acid salt-titanate nanosheet (PAAS/TiNS) nanocomposites is shown in Figure 4.

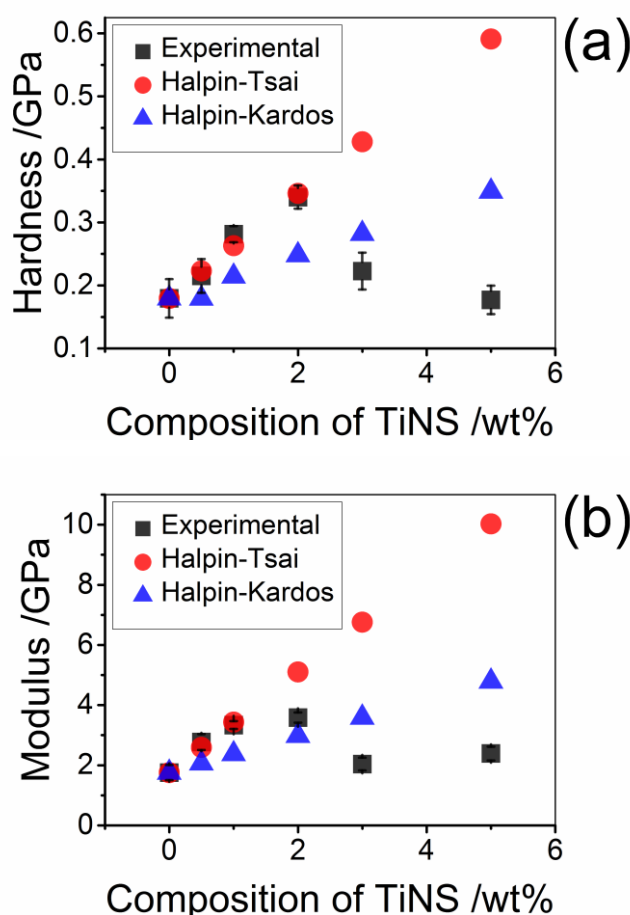


Figure 4. The effect of titanate nanosheets on the mechanical properties of polyamic acid salt compared to the predictions of theoretical models: (A) hardness; (B) modulus.

The addition of titanate nanosheets significantly enhanced the hardness and modulus of water-soluble polyamic acid salt. Hardness increased 90% with addition of 2% TiNS, while the modulus increased 103% compared to the pure polymer. The improvement in hardness follows the Halpin-Tsai theory up to 2 wt% while the modulus follows up to 1 wt%. This might happen due to the nanosheets at low filler concentration being fully exfoliated in Figure 3a) maintaining the same aspect ratio and polymer-filler interaction. Moreover, titanate nanosheets have an anisotropic reinforcement which is highest when the loading is perpendicular to the nanosheet [5]. Figure 3a) shows that most of the nanosheets lay flat on the substrate, rendering them perpendicular to the direction of nanoindentation loading. This is consistent with the Halpin-Tsai theory which assumes that the reinforcement direction is unidirectional to the loading. At higher loading of filler, 'skewed' platelets or tactoid phases were

created (Figure 3b). Such elongated agglomerates may act as short fibres with random orientation, in agreement with the Halpin-Kardos prediction. Similar effects occur with clay fillers [23]. However, experimental results do not follow set theories at higher filler concentration (5 wt%), possibly due to severe agglomerations acting as stress concentration sites [23].

Addition of nanostructures may induce brittleness in polymers [26]. Nanoindentation is also able to give an indication of brittleness via the plasticity index. This index is the ratio of plastic work done on the material to total work (plastic work and elastic work) applied [27]. The index ranged from 0 to 1; brittle materials, such as glass, tend to have low value (0.38) while ductile steel has a higher value (0.72). Table 1 shows that the addition of titanate nanosheets up to 5 wt% did not significantly change the brittleness of polyamic acid salt.

Table 1. Plasticity index of the pure polymer (PAAS) and the composites (PAAS/TiNS) for various loading of TiNS

Sample name	wt% of TiNS	plasticity index
Pure PAAS	0	0.63208
PAAS/TiNS/0.5	0.5	0.691766
PAAS/TiNS/1	1	0.660274
PAAS/TiNS/2	2	0.636735
PAAS/TiNS/3	3	0.622159
PAAS/TiNS/5	5	0.69291

Figure 5 shows that the transparency of polyamic acid salt is reduced when the concentration of titanate nanosheets exceeds 1 wt%. The agglomeration may start to form at a higher titanate loading in Figure 3b) causing scattering of light inside the polyamic acid salt.



Figure 5. A photograph showing the effect of titanate nanosheets on the optical properties of polyamic acid salt (titanate content from left to right: 0, 0.5, 1, 2, 3, 5 wt%)

4. Conclusions

Polyamic acid salt-titanate nanosheet composites have been successfully prepared by solution mixing. Triethylamine (TEA) can be used as a bulky molecule, instead of the more common tetrabutyl ammonium hydroxide, to exfoliate titanate nanosheets. Ultrasonication can assist intercalation of TEA into the nanosheets and their delamination into thin nanosheets. Addition of titanate nanosheet to water soluble polyamic acid significantly enhanced hardness and modulus of the polymer. The hardness increased by 90% on addition of 2% TiNS while the modulus increased by 103% compared to pure polymer. A high aspect ratio ($l/d = 133.33$) and uniform distribution of titanate nanosheets provides significant reinforcement of polymer. This improved behaviour is consistent with Halpin-Tsai theory at low filler content, assuming that the hardness and modulus of titanate nanosheet are the same as TiO_2 . At high filler loading (>2 wt%), the mechanical properties of composites do not fit established theories due to agglomeration of titanate nanosheets. These sheets were stacked on each other, creating several layers of 'skewed' agglomerates or tactoid phases. This causes poor distribution of nanosheets and might disturb stress distribution between nanosheet and polymer. The incorporation of titanate nanosheets has no significant impact on the plasticity of polymer, as indicated by the plasticity index of composite; this assures flexibility of the composites. However, the inclusion of the nanosheets slightly reduces the transparency of polymer, particularly when the titanate nanosheet weight percentage exceeds 1 wt%, due to agglomeration.

Acknowledgements

The authors are grateful to the Indonesian Endowment Fund for Education (LPDP) for funding.

References

-
- [1] Yoshitsugu K *et al* 1993 *J. Mater. Res.* **8** 1185-9.
 - [2] Xin Z *et al* 2010 *Macromolecules* **43** 2357–63.
 - [3] Kirana M S R N *et al* 2011 *Scripta Materialia* **64** 592–5.
 - [4] Lianzhou W and Takayoshi S 2014 *Chem. Rev.* **114** 9455–86.
 - [5] Liu M *et al* 2013 *Nat Commun.* **4** 2029.
 - [6] Marani D *et al* 2010 *Chem. Mater.* **22** 1126.
 - [7] Ratanatawanate C *et al* 2012 *Jr. Mater. Lett.* **66** 242.
 - [8] Harito C *et al* 2017 *Composite Part B: Engineering* **124** 54-63.
 - [9] Halpin J C 1969 *Journal of Composite Materials* **3** 732.
 - [10] Halpin J C and Kardos J L 1976 *Polym. Eng. Sci.* **16** 344-52.
 - [11] Sasaki T and Watanabe M 1998 *J. Am. Chem. Soc.* **120** 4682–9.
 - [12] Grey I E *et al* A 1987 *J. Solid State Chem.* **66** 7–19.
 - [13] Ma R *et al* 2003 *Chemical Physics Letters* **380** 577-582.
 - [14] Ma R *et al* 2005 *J. Phys. Chem. B* **109** 6210-6214.
 - [15] Lee T *et al* 2009 *European Polymer Journal* **45** 19-29.
 - [16] Kreuz, J A *et al* 1996 *J Polym Sci Part A: Polym Chem* **4** 2607–16.
 - [17] Oliver W C and Pharr G M 1992 *J. Mater. Res.* **7** 1565.
 - [18] Paula D R and Robeson L M 2008 *Polymer* **49** 3187–204.
 - [19] Sasaki T *et al* 2001 *J. Phys. Chem. B* **105** 6116–21.
 - [20] Bavykin D V *et al* 2006 *Advanced Materials* **18** 2807–24.
 - [21] Bokobza L 2007 *Polymer* **48** 4907–20.
 - [22] Wan C and Chen B 2012 *J. Mater. Chem.* **22** 3637-46.
 - [23] Ebadi-Dehagani H *et al* 2015 *Composite Part B: Engineering* **69** 133-44.
 - [24] Shackelford J F and Alexander W 2001 *CRC Materials Science and Engineering Handbook* (Boca Raton: CRC Press LLC) chapter 6 474.
 - [25] Goyal R K *et al* 2008 *Materials Science and Engineering A* **491** 230-6.
 - [26] Schadler L S 2004 *Nanocomposite Science and Technology*, ed P M Ajayan P M, Schadler L S and Braun P (Weinheim: Wiley-VCH) 77.
 - [27] Beake B D *et al* 2010 *Nanostructured Thin Films and Coatings: Mechanical Properties*, ed Zhang S (Boca Raton: CRC Press Taylor & Francis Group) chapter 6 206-11.