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Research paper

Development of silane grafted halloysite nanotube reinforced polylactide nanocomposites for the enhancement of mechanical, thermal and dynamic-mechanical properties

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ABSTRACT

In this investigation, halloysite (Hal) nanotubes were surface modified with 3-aminopropyltriethoxysilane (APTES) to enhance the surface interaction of Hal nanotubes with polylactide or poly (lactic acid) (PLA) and to achieve good dispersion of Hal nanotubes across the PLA matrix. Unmodified and silane modified Hal nanotubes were characterized by Fourier transform infrared spectroscopy (FTIR), Nitrogen adsorption-desorption analysis, Thermogravimetric analysis (TGA) and Field emission scanning electron microscopy (FE-SEM) with Energy-dispersive x-ray spectroscopy (EDX) analysis. Nitrogen adsorption-desorption, FTIR and TGA analysis results were confirmed the successful modification of Hal nanotubes surface with APTES. The different wt% of unmodified and APTES modified Hal nanotubes reinforced PLA polymer composites were prepared by using a laboratory scale melt mixer. The resultant Hal-PLA nanocomposites were characterized for their morphology, thermal, mechanical and dynamic-mechanical properties. Tensile strength increased to 62.6 MPa with the addition of 4 wt% of APTES modified Hal-PLA nanocomposites which is 26.5% higher than pure PLA and 15% higher than unmodified (4 wt%) Hal-PLA nanocomposites. Impact strength of 4 wt% APTES modified Hal-PLA nanocomposites was 29.8 MPa, which is 20% higher than the unmodified Hal-PLA nanocomposites and 40% higher than pure PLA. Thermal stability also increased by 17 °C with the addition of 4 wt% of APTES modified Hal nanotubes and 10 °C for the unmodified Hal nanotubes onto PLA. Storage modulus increased >10% with the addition of 4 wt% of APTES modified Hal nanotubes as compared to pure PLA and tan delta values were decreased for the modified Hal nanotubes due to an increase in the compatibilisation between filler and matrix phase. Based on these results, APTES is one of the best choices for the functionalisation of inorganic surface such as Hal nanotubes. The mechanical and thermal properties significantly improved with the addition of a small quantity (4 wt%) of APTES modified Hal nanotubes.

1. Introduction

Since the last few decades, polymeric wastage is on increase due to the extensive usage of synthetically derived polymeric materials in our day-to-day life. Many polymers are non-degradable when they are derived from petroleum resources. Thus, more attention is given to the development of bio-based polymeric materials to overcome the current environmental issues such as global warming, depletion of petroleum resources and environmental pollution. Engineered polymer composites are used in the automotive industry to produce a wide range of automobile components with specific features (low density, high mechanical performance, durability, corrosion resistance, and easy processing) which metals and alloys cannot easily offer (Notta-cuvier et al., 2014).

PLA is a biodegradable polymer derived from renewable sources such as corn starch and sugarcane (Pandey et al., 2005; Lim et al., 2008). It draws more interest owing to its renewability, biodegradability, biocompatibility and good mechanical properties (Raquez et al., 2013). Moreover, PLA degradation releases non-toxic gases at a lower level (Nel, 2007). Besides, for packaging, automotive, and electronic applications it has comparable tensile strength and Young's modulus with several commercial polymers such as polypropylene, polyethylene, polystyrene etc. (Notta-cuvier et al., 2014). However, PLA has limitations of low thermal stability, low toughness and extreme brittleness (Pandey et al., 2005; Lim et al., 2008). It is therefore necessary to reduce the brittleness and to improve the mechanical and thermal properties of PLA when we aim for long-term applications more importantly on a large scale (Raquez et al., 2013).

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It has already been proved that the incorporation of nanofillers onto the PLA matrix increases crystallization ability, elongation and thermal properties. The incorporation of exfoliated graphite onto PLA matrix increased the tensile strength and thermal stability by 12% and 14 °C respectively as compared to pure PLA (Kim and Jeong, 2010; Evagelia et al., 2011). Introduction of a smaller amount (0.2 wt%) of carbon nanotubes (CNT) as nanofillers into PLA enhanced the tensile strength and modulus by 25% and 12% respectively (Park et al., 2013). However, nanofillers such as graphene, CNT, fullerenes and oxide nanoparticles are toxic to the environment and therefore using them as fillers in the polymer matrix again causes pollution (Nel, 2007).

The clay based nanofillers as plasticizer are good substitutes which also improved the thermal properties of PLA >20% as compared to pure PLA (Liu et al., 2013). Aluminosilicate-based nanofillers are also widely used in the clay polymer nanocomposites (CPN) to enhance the mechanical and thermal properties. Aluminosilicates are also called as layered silicate nanocomposites which are a new class of hybrid materials, making them more interesting in academic and industrial realms due to their excellent thermal barrier, thermo-mechanical and fire-resistance properties which have been achieved at a lower content (˜5 wt%). However, improvements in the desired properties rely on how well the dispersion of nanofillers within the polymer matrix (Sinha Ray and Okamoto, 2003).

Hal nanotubes are naturally occurring aluminosilicates with the formula, $Al_2Si_2O_5\,(OH)_4 \cdot nH_2O$. Their tubular structure in nano dimension with high aspect ratio make them as unique materials to be used as fillers in the generation of CPN. Hal nanotubes are chemically similar to kaolinite group which consist of multiple layer of hollow cylinders with nanometer dimensions (Joussein et al., 2005). Hal nanotubes consist of gibbsite like array of aluminol groups (Al-OH) which are located inside the lumen while the outer surface covered with the siloxane (Si-O-Si) groups. These two unit layers are separated by a barrier of water molecules which lead to hydrated Hal nanotubes with a basal spacing of 10 Å which is larger than that of kaolinite (~3 Å) (Yuan et al., 2008, 2015). Hal nanotubes are naturally formed in the earth crust over millions of years and having unique and versatile mechanical and thermal properties (Du et al., 2010; Rooj et al., 2010). However, the presence of a large number of hydroxyl groups on the surface of Hal nanotubes leads to more hydrophilic nature. This hydrophilic nature of Hal nanotubes have very limited applications to use them as fillers in the generation of CPN (Yuan et al., 2008; Pasbakhsh et al., 2010; Jin et al., 2015).

In recent times, a sizeable number of reports being published on Hal nanotubes reinforced CPN (Liu et al., 2014). The loading of Hal nanotubes into PLA matrix significantly improved the mechanical properties. Tensile and flexural strength increased by 34% and 25% respectively with the addition of 30phr of unmodified Hal nanotubes into PLA as compared to pure PLA. Thermal stability of 30phr loaded unmodified Hal-PLA nanocomposite was slightly increased by 4.4 °C as compared to pure PLA (Liu et al., 2013). However, similar to other nanoparticles, dispersion of Hal nanotubes into polymer matrix is challenging (Kim and Jeong, 2010; Raquez et al., 2013). Modification or functionalization of nanofillers is a way to enhance their dispersion into the polymer matrix. Functionalization of Hal nanotubes can enhance the surface properties and leads to good dispersion into PLA matrix of CPN. Surface modification of Hal nanotubes with different types of silane coupling agents is the most common method to improve the surface properties of Hal nanotubes. This method is referred as the grafting of silanes and is carried out via condensation between hydrolysed silanes and surface hydroxyl groups of Hal nanotubes. The modification of Hal nanotubes with silane coupling agent enhanced the dispersion of Hal nanotubes into natural rubber (NR) matrix and improved the thermal stability by 64 °C as compared to unmodified Hal nanotubes (Rooj et al., 2010). The modified Hal nanotubes with silane coupling agent enhanced their dispersion in Ethylene propylene diene monomer (EPDM) matrix and increased the mechanical properties. 30phr of silane modified Hal nanotubes into EPDM matrix increased the tensile strength, modulus and elongation at break by 360%, 65% and 135% respectively as compared to unmodified Hal-EPDM composites (Pasbakhsh et al., 2010).

The aim of this investigation is to study the surface morphology and thermal stability of unmodified and APTES modified Hal nanotubes using SEM with EDX analysis, N_2 adsorption-desorption analysis, FTIR analysis and TGA analysis. The investigation also includes the study of the effect of silane functionalised Hal nanotubes on the morphology, mechanical, dynamic mechanical and thermal properties of Hal-PLA nanocomposites. For this, different wt% of untreated and silane treated Hal nanotubes reinforced PLA nanocomposites were prepared and the surface morphology, tensile strength, modulus, percentage elongation, viscoelastic and thermal properties were studied.

2. Experimental

2.1. Materials

PLA (trade name of Ingeo™ 2003D) was supplied by NatureWorks Inc., USA. The melt index was 6 g/10 m (210 °C, 2.16 kg). Hal nanotubes were purchased from Sigma-Aldrich, Malaysia. 3-Aminopropyltriethoxysilane (APTES) was supplied by Fisher Scientific, Malaysia. All the materials were used as received without any further purification.

2.2. Modification of Hal nanotubes

The functionalisation of Hal nanotubes was carried out with the silane coupling agent, APTES. The amount of APTES was determined by using the Eq. (1) (MacMillan, 2009) to ensure the uniform distribution of silane onto the surface of Hal nanotubes. Typical surface area of Hal nanotubes is 65 m^2/g and the specific surface area of APTES is 355 m^2/g (Arkles, 1977).

$$\text{Amount of APTES (g)} = \frac{\text{Amount of Hal (g)} \times \text{surface area of Hal } (m^2/g)}{\text{Specific surface area of APTES } (m^2/g)} \tag{1}$$

12 g of silane coupling agent i.e. APTES was dissolved in 500 mL of ethanol (95%) solution and 1 mL of acetic acid was added to keep the pH between 4.5 and 5.5. This solution was then stirred vigorously at 60 °C for 15 min. 50 g of Hal nanotubes were added to the solution and stirred at 60 °C for 2 h. The silane modified Hal nanotubes were then filtered and washed with ethanol and dried at room temperature for 24 h and then dried under vacuum at 100 °C for 8 h to remove the moisture and ethanol (Arkles et al., 1992; Du et al., 2006).

In case of Hal nanotubes, the aluminol groups (Al-OH) on the surface of the inner layer of Hal nanotubes have high degree of chemical reactivity with organic compounds such as APTES (Scheme 1). Yuan et al. (2008) investigated the modifications of Hal nanotubes with APTES by grafting on the inner surface of Hal nanotubes. The external surface of Hal nanotubes consists of siloxane (*Si*-O-Si) groups and few aluminols (Al-OH) and silanols (Si-OH) at the edges and surface defects of Hal nanotubes. They reported that the amino-propyl groups as well as the hydroxyl groups of the hydrolysed APTES formed the covalent bonds between Al-OH groups of the inner surface of Hal nanotubes and the siloxane (Si-O-Si) groups at the edges or the surface defects of Hal nanotubes (Yuan et al., 2015). On the other hand, since the modification of Hal nanotubes was carried out using the mixture of water and ethanol solution, some of the hydrolysed APTES reacts with each other to form oligomers which grafted by hydrogen bonding. These oligomers were further reacted with aluminols and siloxanes to form the cross-linked network in the lumen of Hal nanotubes (Arkles et al., 1992; Yuan et al., 2008). More hydroxyl groups exist on the surface of Hal nanotubes due to surface defects. These hydroxyl groups are the potential reactive sites for the surface modification on the external surface of Hal

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