Effect of Filler Content and Chemical Modification on Mechanical Properties of Polylactic Acid/Polymethyl Methacrylate/Nypa Fruticans Husk Biocomposites

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Abstract. The main purpose of incorporating Nypa fruticans husks (NFH) into Polylactic acid (PLA)/Polymethylmethacrylate (PMMA) is to decrease the costs and enhanced the properties of the biocomposites. 3-Aminopropyl Triethoxysilane (3-APE) was used as coupling agent. The effect of NFH content and 3-APE on the mechanical properties and morphology of the biocomposites were investigated. Results show that the effect of NFH content increased Young’s modulus but decreased the tensile strength and elongation at break of PLA/PMMA/NFH biocomposites. However, silanized biocomposites using 3-APE was found to enhanced the tensile strength and Young’s modulus but decreased the elongation at break of the silanized biocomposites. Scanning electron microscopy (SEM) study of the tensile fracture surface of the biocomposites indicated that the used of 3-APE as coupling agent improved the interfacial interaction between NFH and PLA/PMMA blends.

1. Introduction

Plastic materials have found wide applications in every aspect of life and industries. However, most of the conventional plastics are nonbiodegradable, and their accumulation in the environment has been a threat to the planet. Environmental concerns and a shortage of petroleum resources have driven efforts aimed at the production of biodegradable materials [1].

The use of inorganic fillers is a usual practice in the plastics industry to improve the mechanical properties of thermoplastics, which are commonly known as polymer composites. These materials usually comprise of an effective polymeric matrix in which fibers or small filler particles are thoroughly dispersed in composite systems. The filler must be well dispersed in the matrix to avoid zones of weaker cohesion where flaws and other defects will be initiated upon stressing [2].

Nypa Fruticans (NF) is a monoecious palm with special characteristics. In Malaysia, NF palm can be found throughout the year and it can be considered an abundant source. [3]. Nypa, consisting of frond, shell, husk, and leaf, was chemically characterised for cellulose, hemicellulose, lignin, starch, protein, extractives, and inorganic constituents for its each part [4].

Polylactide (PLA) is biodegradable and biocompatible thermoplastic which can be fermented from renewable resources. It has proved to be a cost-effective alternative to traditional, commodity plastics for various end-use applications, due to its good mechanical properties, thermal plasticity, and facile fabrication [5]. Together with its biodegradable and compostable properties, PLA in principle holds...
great potential as an alternative to petroleum-based polymers. However, some of its applications are limited by its low elongation at break and poor toughness. PLA has a glass transition temperature ranging from 55 °C to 65 °C, and it is brittle at room temperature, fracturing via a crazing mechanism. To modify the mechanical brittleness of PLA, many strategies such as processing manipulation, copolymerization and blending have been employed [6]. Several approaches based on (nano)composites or direct chemical modifications of the polyester chains were previously explored [7–11], but melt-blending of PLA with synthetic and, at least, potentially/partly bio-based thermoplastic polymers represents a more robust and easy route for these technical applications. Among them, poly(methyl methacrylate) (PMMA) with its intrinsic high mechanical properties, high transparency, UV resistance and long-term stability is a serious candidate. Literature about PLA/PMMA blends is composed of several articles, each of them using different preparation techniques, conditions and raw materials, highlighting some tricky conditions to obtain PLA/PMMA miscibility. Miscibility in poly(lactic acid)/PMMA blends was first mentioned by Eguiburu et al. [12].

A coupling agent is a chemical that functions at the interface to create a chemical bridge between the filler and matrix. In order to enhance the behavior of these biocomposites, NFH have treated with 3-APE. The 3-APE has ethoxy groups that hydrolyzed in water or solvent producing silanol and next the silanol reacts with OH group of filler which form stable covalent bond onto the filler surface. Generally, the coupling agent improves the degree crosslinking in the interface region and offers a suitable bonding result, as well as creation of high filler surface area. The amine group from 3-APE can form hydrogen bonds to COO- sites on hydrolyzed PLA backbone [13].

In the present study the effect of NFH content and the silane coupling agent on mechanical properties and morphology of PLA/PMMA/NFH biocomposites were investigated.

2. Experimental
2.1. Materials
PLA supplied by TT Biotechnologies Sdn. Bhd, Penang and PMMA obtained from SLT Plastic Sdn. Bhd, Penang. The NFH was obtained from Kota Kayang, Perlis. The NFH was cleaned and dried at 80°C for 24 hours in an oven. Nypa fruticans was then crushed into small pieces and ground to a powder. The average particle size of NFH was below 75μm determined by using a sieve. 3-aminopropyl triethoxysilane (3-APE) was supplied by Fluka, Penang A subsubsection. The paragraph text follows on from the subsubsection heading but should not be in italic.

2.2. Filler Treatment
The silane coupling agent (3-APE), was dissolved in 3% (v/v) ethanol solution at room temperature. The NFH was slowly transferred into the 3-APE solution and stirred for 1 hour. The NF was filtered using filter paper and dried at 80 °C for 24 hours.

2.3. Preparation of Biocomposites
PLA/PMMA/NFH biocomposites were prepared using a twin-screw extruder. The biocomposites were extruded at 180 °C to 250 °C, feeder screw of 8 rpm and screw speed of 80 rpm. First, PLA and PMMA were inserted into the hopper until completely melted. The melted polymer were then extruded and pelletized. The pellets were then dried in an oven at 80 °C for 24 hours to remove moisture.

The extrudate biocomposites were compressed using compression moulding machine, model GT 7014A. The compression was done at 180 °C with 4 min preheating, 2 min compression, and subsequent cooling for 4 min. A similar procedure was done for silanized PLA/PMMA/NFH biocomposites. Table 1 shows the formulation for untreated and treated PLA/PMMA/NFH biocomposites.
Table 1. Formulation of Untreated and Treated Biocomposites.

| Material  | Untreated | Treated  |
|-----------|-----------|----------|
| PLA (php) | 70        | 70       |
| PMMA (php)| 30        | 30       |
| NFH (php) | 0, 10, 20, 30, 40 | 10, 20, 30, 40 |
| 3-APE (%) | -         | 3        |

*php = part per hundred of total polymer

2.4. Tensile Properties
Tensile tests were carried out according to ASTM D638 using an Instron 5569. The crosshead speed for the biocomposites testing was 20 mm/min. An average of five samples for each formulation was tested. Tensile strength, elongation at break and Young’s modulus were recorded and calculated by the instrument software.

2.5. Morphological Studies
The morphological study of the tensile fractured surfaces of the biocomposites was carried out using a scanning electron microscope (SEM), model JSM 6260 LE JOEL. The fractured ends of specimens were mounted on aluminium stubs and sputter coated with a thin layer of palladium to avoid electrostatic charging during examination.

3. Result and Discussion
The addition of NFH to the PLA/PMMA matrix resulted in changes of the tensile properties. The effect of NFH content on the tensile strength of untreated and treated PLA/PMMA/NFH biocomposites is illustrated in Figure 1. It can be seen that tensile strength of untreated PLA/PMMA/NFH biocomposites decreased with an increase of NFH content. Many studied reported that the tensile properties of the composites generally become poorer as the content of natural filler increased. The incorporation of NFH reduced the tensile strength due to poor adhesion between NFH and PLA/PMMA matrix. However, the treated biocomposites with 3-APE had higher tensile strength compared to untreated biocomposites. The increased in tensile strength of the silanazed biocomposites attributed by improved interfacial adhesion between NFH and PLA/PMMA matrix. The improved interfacial adhesion due to chemical bonding between the hydrophobic part of the silane on the NFH surface and PLA/PMMA matrix or van der Waals forces between them.

![Figure 1. Effect of NFH content on tensile strength of untreated and treated PLA/PMMA/NFH biocomposites.](image-url)
The effect of NFH content on elongation at break of untreated and treated PLA/PMMA/NFH biocomposites is present in Figure 2. The elongation at break of the untreated PLA/PMMA/NFH biocomposites decreased as the NFH content increased. The decreased of elongation at break may be attributed to a reduction in deformability of the rigid interface between fillers and matrix. The silanized biocomposites treated with 3-APE show lower elongation at break compared to untreated biocomposites. The silane treatment has increased the tensile strength of biocomposites with the enhancement in rigidity and decrement of the ductility of biocomposites, which consequently lowered the elongation at break of the biocomposites.

Figure 2. Effect of NFH content on elongation at break of untreated and treated PLA/PMMA/NFH biocomposites

Figure 3 illustrate the effect of NFH content on the Young’s modulus of untreated and treated PLA/PMMA/NFH biocomposites. The result showed that the Young’s modulus of untreated biocomposites increased with NFH content increases. Generally, filler that had higher stiffness than the matrix increased the Young’s modulus of the biocomposites and reduced the elongation at break. The increasing of NFH content potentially increased the filler-matrix interaction, which led to higher efficiency of stress transfer from matrix to filler phase, thus increasing the Young’s modulus. At similar NFH contents, treated biocomposites had higher Young’s modulus than untreated biocomposites. It can be seen that the Young’s modulus of treated biocomposites were increased slightly by silane treatment. The increases of Young’s modulus of the silanized biocomposites were most likely caused by improved interfacial adhesion between the NFH filler and PLA/PMMA matrix.

Figure 3. Effect of NFH content on Young’s modulus of untreated and treated PLA/PMMA/NFH biocomposites
The SEM micrographs of the tensile fracture surfaces of untreated and treated PLA/PMMA/NFH biocomposites with silane coupling agent at 20 and 40 php NFH content were shown in Figure 4 and 5, respectively. The micrographs of the untreated biocomposites showed poor interfacial adhesion and dispersion of NFH content in the PLA/PMMA matrix and also exhibit NFH detachment and pull out from the matrix. Meanwhile, the micrographs of treated PLA/PMMA/NFH biocomposites showed good interfacial bonding between the PLA/PMMA matrix and NFH. Moreover, the surface morphology of treated PLA/PMMA/NFH biocomposites exhibits less NFH detachment and pull out from the PLA/PMMA matrix. It was apparent that the presence of 3-APE silane led to better interfacial interaction between NFH and PLA/PMMA matrix.

![Figure 4: Scanning electron micrograph (SEM) of untreated PLA/PMMA/NFH biocomposites (a) (20 php of NFH) & (b) (40 php of NFH)](image)

![Figure 5: Scanning electron micrograph (SEM) of treated PLA/PMMA/NFH biocomposites (a) (20 php of NFH) & (b) (40 php of NFH)](image)

4. Conclusion
The effect of NFH content had increased Young’s modulus of the biocomposites, but decreased the tensile strength and elongation at break. The presence of silane coupling agent (3-APE) increased the tensile strength and Young’s modulus but decreased the elongation at break of treated PLA/PMMA/NFH biocomposites. SEM micrographs of tensile fracture surface of silanized biocomposites indicated the improved of interfacial interaction between NFH and PLA/PMMA matrix.

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