The Effect Of Filler Content and Chemical Modification On The Properties Of Poly(Lactic Acid)/Pandanus Amaryllifolius Biocomposite Films

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Abstract. The biocomposite films of Polylactic acid (PLA) and Pandanus Amaryllifolius filler (PAF) were prepared using solvent casting method. The effect of PAF content and modification of PAF by silane coupling agent on mechanical, morphological and enzymatic biodegradation of PLA/PAF biocomposite films were determined. PAF content in PLA/PAF biocomposite films caused the tensile strength and elongation at break to decrease, meanwhile Young’s modulus of biocomposite films increased. The SEM micrographs showed poor filler-matrix interaction between PAF and PLA matrix by showing rough surface morphology. The chemical modification of PAF using 3-APE silane coupling agent improved Young’s modulus and tensile strength in biocomposite films however elongation at break has exhibited the trend of decrease. The morphological studied showed that modified PAF had better dispersion and interaction with PLA matrix by showing smoother surface morphology. The changes of functional group of unmodified and modified biocomposite films were proven by Fourier Transform Infrared study.

1 Introduction

PLA is one of the biodegradable and biocompatible thermoplastics that could be formed by fermentation from sustainable and renewable resources [1]. Nowadays, PLA has become an alternative to petrochemical polymer for various applications. Main application of PLA today is in packaging field due to its rigidity, clarity and ease of processing [2]. Resistance of PLA towards aliphatic molecules also one of the properties attributes to food packaging field. PLA can easily process into desired configuration such as moulded part and films by using conventional thermoplastic processing techniques. However, low impact resistance and brittle feature has restricted the use for application which require higher stress level [3]. To

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overcome these limitations, reinforcing filler can be added to PLA to enhance its mechanical properties. Nowadays, natural filler is getting more focused due to its biodegradability, light weight, less abrasiveness and its high specific strength comparing with synthetic filler [4]. The properties of natural fillers depend on several factor such as growing condition, region of origin chemical composition, structural and other characteristics [5]. Thus, there is a need to master more knowledge and have a well usage of them because these will affect the desired properties of biocomposites [6]. Jute [7], kenaf [8], abaca [9], bamboo [10], flax and Cordenka [11] have been extensively investigated by material scientists around the world and used as filler for biocomposites variety of applications.

Pandanus amaryllifolius filler (PAF) or commonly known as Pandan leaves is widely distributed in parts of south-eastern Asia like Malaysia, Thailand and Indonesia [12]. PAF was applied due to its high fibre contents, low prices and high strength. Besides that, PAF has been reported to be one of the best 2-acetyl-1-pyrrolin (2-AP) sources [13]. The colour and unique aroma from 2-AP contribute to a creative composite packaging with a unique Pandan aroma.

However, natural fillers are hydrophilic, which is incompatible with hydrophobic nature of PLA. This will result in poor interfacial adhesion between filler and matrix. Poor interfacial adhesion of filler-matrix will affect the physical and mechanical properties of biocomposites [14]. Furthermore, the hydroxyl groups which are rich in the surface of natural filler will also cause moisture uptake from the environment too. Therefore, chemical modification has been to done on natural fillers to increase the compatibility and interaction with the matrix.

This work was focused on the effect of PAF content and chemical modification of PAF on the mechanical properties and morphological properties of biocomposite films. Biodegradability of biocomposite films were tested by enzymatic biodegradation test. FTIR was utilized to determine the change in functional group for PLA /PAF biocomposite films.

2 Methodology

2.1 Materials

Polylactic acid was supplied from TT Biotechnologies Sdn Bhd., Penang. Whereas chloroform, ethanol 95% were purchased from HmbG chemicals, Syarikat Saintifik Jaya, Malaysia. 3-Aminopropylethoxysilane (3-APE) was supplied by Fkuka, Penang. Pandanus Amaryllifolius filler (PAF) was obtained around Perlis. PAF was first cleaned and dried in oven at 80 °C for 24 hours. The dried PAF were then grounded to fine powder, sieved by scientific siever to obtain 53μm particle size.

2.2 Methods

2.2.1 Chemical Modification of Pandanus

3-APE was dissolved in ethanol 3:1 v/v at ambient temperature. After that, PAF were added into the silane solution and stirred for 1 hour by mechanical stirrer. Mixture was left overnight. The PAF was filtered by Whatman filter paper and dried in the oven at 80 °C overnight.
2.2.2 Preparation of PLA/Pandanus biocomposites films

Pellets of PLA were dissolved in 100ml chloroform and stirrer in water bath at 45°C. The mixture were stirred at 1 hour at 350rpm to make sure PLA pellets completely dissolved. Once PLA was completely dissolved, Pandanus were loaded constantly. The mixture was placed in water bath at 45°C and stirred for another 1 hour by mechanical stirrer. PLA/PAF solution was casted into a clean glass mould and left for 2 days at ambient temperature. The dried films was gently been removed from the glass mould. Same procedure was repeated for chemical modification of PLA/PAF biocomposite films. The biocomposites were compounded followed the formulation as shown in Table 1.

Table 1. Formulation of PLA/PAF biocomposite films.

| Materials        | Unmodified PLA/PAF biocomposite films | Modified PLA/PAF biocomposite films |
|------------------|---------------------------------------|------------------------------------|
| PLA (php)        | 100                                   | 100                                |
| PAF (php)        | 0,5,10,15,20,25                        | 5,10,15,20,25                      |
| 3-APE (%)        | -                                     | 3                                  |

2.3 Testing and Characterization

2.3.1 Tensile Test

Tensile test of biocomposite films were carried out by using Instron Machine 5960 Series followed ASTM D 882. The sample was been prepared in rectangular shape. Crosshead speed set was 20mm/min. Tensile strength, elongation at break and Young’s modulus were obtained for each tested specimen.

2.3.2 Morphological Analysis

Scanning Electron Microscopy (SEM) with the model of JEOL-6400-LA was applied to study the tensile fracture surface and morphology of biocomposite films. Tensile fracture end of specimens was mounted onto aluminium stubs and a thin layer of palladium was sputter-coated to prevent from electrostatic charging during observation. The SEM micrographs were obtained at 10Kv.

2.3.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR was used to characterize the presence of functional groups for unmodified PAF and modified PAF. The analysis was carried out by using the FTIR spectra resulted from the Perkin Elmer, Model L 128044. The range of scanned was set between 400 and 4000cm⁻¹ with a resolution of 4cm⁻¹.

3 Result & Discussion

3.1 Tensile Properties

Fig. 1 demonstrated the effect of PAF content on tensile strength of unmodified and modified PLA/PAF biocomposite films. It can be seen that tensile strength of unmodified and modified biocomposite films decreased as PAF content increased. However, biocomposite films which
undergo silanization demonstrated a higher tensile strength in comparison with unmodified biocomposite films. The increased in tensile strength was resulted from enhancement of interfacial adhesion between PLA matrix and PAF. Proper wetting between filler and matrix lead to formation of better filler-matrix interface and van der Waals forces between them [16]. Jandas et al. (2011) also reported that chemical treatment of banana fibre (BF) will result in an improvement in interfacial bonding of the fibres with the PLA matrix. This is predominantly due to formation of a bridge between fibre and matrix and shows the improvement of the interaction for filler and matrix. Hence, it showed the trend of improvement in the tensile strength treated biocomposites [17].

![Fig. 1. Effect of PAF content on tensile strength of unmodified and modified PLA/PAF biocomposite films with 3-APE.](image)

Fig. 2 illustrated the effect of 3-APE on elongation at break of unmodified and modified PLA/PAF biocomposite films. It had found that the increased in PAF content had decreased elongation at break for unmodified and modified PLA/PAF biocomposite films. This is because PLA matrix and PAF experienced a decreased in deformability of rigid interface. The movement of PLA chains aligned during elongation had been restricted. At similar PAF content, the modified biocomposites had shown lower elongation at break in comparison with unmodified biocomposites. After silane treatment, tensile strength of biocomposites had an improvement in rigidity and decrement in ductility, which consequently lower elongation at break of PLA/PAF biocomposite films. Similar observation was reported by Syahmie et al. (2015) which was focused on silane treatment of Nypa Fruticans husk filler and the elongation at break of biocomposites was reduce due to the decrement of ductility [18]. Hence, it had shown that chemical modification of filler will enhance interfacial attraction and driven to lower mobility of the polymer chain.
Fig. 2. Effect of PAF content on elongation at break of unmodified and modified PLA/PAF biocomposite films with 3-APE.

Fig. 3 shows the effect of PAF content on Young's modulus of unmodified and modified PLA/PAF biocomposite films with silane coupling agent. Unmodified and modified PLA/PAF films exhibited an increase of Young’s modulus in comparison with neat PLA. However, modified PLA/PAF biocomposite films exhibited a higher increment than unmodified PLA/PAF biocomposite films. 3-APE treatment on PAF had increased the Young's modulus of the PLA/PAF biocomposite films. This indicated that the chemical modification of PAF has led to a better and higher efficiency of load transfer which provide for better continuity and a stronger interface between the matrix and natural filler [19]. 3-APE has the ability to interact with polylactide chain which was crucial to make it compatible with PAF. Silane can contribute to the interface with hydrophilic properties, the molecule of silane had bifunctional groups which make them capable to form a bridge with the hydrophilic and hydrophobic phase. During the modification, 3-APE was hydrolysed to silanol, which can form bonding effectively with carboxylic groups of PAF through ester linkage. Amino group which contain in 3-APE can also form hydrogen bonds with C=O sites on the PLA backbone. Hence, this led to compatible of PAF with the PLA matrix [17]. Same result in PLA/durian ring cellulose were found by P Penjumeas et al. (2016). Previously worked by Syahmie et al. (2015), it can be seen that Young’s modulus of treated PLA/rLDPE/NFF biocomposites were increased slightly by silane treatment compared to untreated PLA/CSP biocomposites. It shows interfacial adhesion between NFF filler and PLA inherent in the mobility of the polymer chain [18].
3.2 Morphological Analysis

Fig. 4(a) illustrates the micrograph of tensile fracture surface of PLA/PAF biocomposite films at 10 php of PAF while Fig. 4(b) shows the micrograph of tensile fracture of 20php of PAF. From the Fig. 4(b) the micrograph shows rougher microstructure compare to the microstructure in Fig. 4(a). Notable gaps had been displayed between PLA matrix and filler. The presence of gaps attributed to the debonding during tensile test or poor dispersion during biocomposite preparations which indicated a weak filler-matrix interaction. The poor interfacial interaction between PLA matrix and PAF filler also resulted in filler pulled out during tensile test. In addition, filler agglomeration and poor dispersion has shown in Fig. 4(b). This is because higher PAF content led to tendency of filler-filler interaction to form agglomerate and poor dispersion. The micrographs of tensile fracture surface of modified PLA/PAF biocomposite films with 3-APE silane coupling agent were shown in Fig. 5(a) and (b). The micrograph of modified PLA/PAF biocomposite films exhibited a smooth surface and significantly voids had been reduced compared to unmodified PLA/PAF biocomposite films. Moreover, at higher filler content as illustrated in Fig. 5(b), PAF well embedded and created interlocking mechanism with the surface of PLA matrix. This is because modified PLA/PAF biocomposite films had good interfacial interaction between matrix of PLA and PAF. Silanization of filler modified its surface properties and lead to improvement the filler-matrix interaction rather than filler-filler interaction. The improvement in interfacial adhesion led to better stress transfer from the PLA matrix to PAF which result in better tensile performance compared to unmodified PLA/PAF biocomposite.

![Fig. 3. Effect of PAF content on Young’s modulus of unmodified and modified PLA/PAF biocomposite films with 3-APE.](image-url)
Fig. 4. Scanning electron micrograph of unmodified PLA/PAF biocomposite films (a) 10 php of PAF and (b) 20php of PAF.

Fig. 5. Scanning electron micrograph of modified PLA/PAF biocomposite films (a) 10 php of PAF and (b) 20 php of PAF.

3.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectra of unmodified PAF and modified PAF/PLA biocomposite films was shown in Fig. 6. The spectra of biocomposite specimen is assumed to include a combination of PLA and filler transmittance peak. From the spectra of unmodified PLA/PAF, the peaks at the 1752.14 cm\(^{-1}\) in the C=O stretching region, peak at 1191.30 cm\(^{-1}\) in C-H bending region and the peak at 1085.60 cm\(^{-1}\) in C-O stretching region indicated the peak for between PLA. Meanwhile, for modified PLA/PAF spectra, peak at 1752.27 cm\(^{-1}\) in C=O stretching region, 1190.94 cm\(^{-1}\) in C-H bending region and 1085.73 cm\(^{-1}\) in C-O stretching region represented the peak for PLA. It can be seen on the IR spectrum of unmodified PLA/PAF biocomposite at peak 3302.70 cm\(^{-1}\) assigned to hydroxyl group (O-H) belonging to PAF. The peak at 2994.35 cm\(^{-1}\) assigned to C-H stretching vibration. Besides, carbonyl group (C=O) from hemicellulose was shown at 1752.14 cm\(^{-1}\). While 1450.80 cm\(^{-1}\) peak indicated C-H deformation from lignin. Cellulose and lignin attributed to peak at 1369.4 cm\(^{-1}\). Furthermore, the peaks in the range of 1000-1150 cm\(^{-1}\) were C-O-C and C-O groups from main carbohydrates of cellulose and lignin. The peaks at 700-900 cm\(^{-1}\) were attributed to C-H vibration. The modified PAF found that the IR spectrum has a significant decreased from 3302.70 cm\(^{-1}\) to 3249.84 cm\(^{-1}\). This is well agreed for the formation of hydrogen bond from the interaction of hydroxyl group in PAF and polar group of 3-APE. Peak at 692.33 cm\(^{-1}\) corresponding to Si-O-C bending in 3-APE.
4 Conclusion

Tensile strength and elongation at break of PLA/PAF biocomposite films decreased with increased in PAF content. However, there was an increase in Young’s modulus with increasing in PAF content. The morphological studied of tensile fracture surface showed poor interfacial interaction between hydrophobic PLA matrix and hydrophilic PAF. The chemical modification using 3-APE silane coupling agent, modified PLA/PAF biocomposite films exhibited higher tensile properties in terms of tensile strength and Young’s modulus. However, elongation at break demonstrated lower value due to restriction in mobility of PLA chains. The SEM micrograph of modified PAF showed good dispersion and high compatible of PAF in the PLA matrix. Furthermore, FTIR anlaysis observed hydroxyl groups on PAF had decreased due to reaction of 3-APE with PAF.

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