Chemical Modification of Palm Kernel Shell Filled Polylactic Acid Biocomposite Films

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Palm kernel shell (PKS) was incorporated with polylactic acid (PLA) using a solution casting method to produce PLA/PKS biocomposite films. The effects of filler content and butyl methacrylate on the mechanical properties, morphological properties, and thermal properties of PLA/PKS biocomposite films were studied. The addition of PKS into the PLA matrix decreased the tensile strength and elongation at break of PLA/PKS biocomposite films with increasing filler content. In contrast, the modulus of elasticity of the biocomposite films increased. The use of butyl methacrylate as a chemical modification for PKS enhanced the interfacial adhesion and wettability of PKS inside the PLA matrix. This effect was confirmed by the increase in tensile strength, modulus of elasticity, and thermal stability of the biocomposite films. Moreover, scanning electron microscopy showed that there was better interfacial interaction between the filler and the PLA matrix.

*Keyword**:** Polylactic acid; Palm kernel shell; Butyl methacrylate; Biocomposite films*

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INTRODUCTION

A main concern about the disposal of plastics is their lack of biodegradability. Due to this issue, new biodegradable polymer biocomposites have been developed from renewable resources (Plackett and Sodergard 2005). There are many limitations that restrict the usage of biodegradable polymers as composite matrices. Most research focuses on using thermoplastics and thermoset as composite matrices because biodegradable polymers are expensive and not readily available. Moreover, petroleum-based polymers are often more commonly used than biopolymers that are environmental friendly, such as polylactic acid (PLA).

Polylactic acid (PLA) is an aliphatic polyester that is synthesized using biobased materials from agro-resources (Niounakis 2013). The main advantages of using PLA as a matrix in polymer composites are its renewability, biocompatibility, energy savings, and processability (Rasal *et al.* 2010). PLA is renewable and degradable because it is derived from cornstarch, a biobased material that releases primarily H_2O and CO_2 as by products during its degradation, which are not harmful to the human body and the environment. As such, PLA is an excellent material for biomedical and food packaging applications (Bergsma 2005). Moreover, PLA can be processed using extrusion, blow molding, and film casting because it has great thermal processibility compared with other biomaterials, such as poly(ethylene glycol) (PEG), poly(hydroxyalkanoates) (PHAs), and poly(e-caprolactone) (PCL) (Rhim 2006).

The incorporation of natural fibres inside polymer matrices offers great advantages such as reduced costs, natural abundance, low density, and high specific properties, and less residue for incineration (Bledzki *et al.* 2002; Evans *et al.* 2002; Sapuan and Maleque 2005; Leman *et al.* 2008). Palm oil and palm kernel oils that are extracted from the outer and inner cores of palm nuts. The palm kernel shell (PKS) is covered by a hard endocarp, which is also known as oil palm kernel shell (OPKS) or oil palm shell (OPS). Some emerging issues related to the oil palm industry may affect the environment and growing economies. A total of 80% of the material is removed as waste after processing of the fresh fruit bunches, and 6.89 million tons of PKS are produced annually, which is expected to increase in the future (Chong *et al.* 2013). PKS is occasionally used as boiler fuel, and the incorporation of PKS inside polymeric materials may improve the mechanical properties of composites (Nabinejad *et al.* 2014).

Structurally, PKS is composed mainly of lignin and hemicellulose; it contains 54% lignin, which is higher than other shell residues such as coconut shell (ECN 2008). PKS mainly consists of lignin (53.85%), cellulose (6.92%), and hemicellulose (26.16%) (Dagwa *et al.* 2014). Surface modification is one of the crucial processing steps in the development of biopolymer composites. Generally, the main disadvantage of natural fibres is that they have highly hydrophilic properties, whereas the polymer matrix tends to have hydrophobic properties. This causes poor interfacial interactions between the two and, as a result, poor end properties of the materials. Surface modification is one of the techniques needed to facilitate the fibre dispersion onto the matrix and improve the fibre-matrix interaction (Netravali 2007). Some of the techniques that improve fibre-matrix adhesion include fiber bleaching, acetylation, esterification, grafting of monomers, and the use of bi-functional molecules (Belgacem and Gandini 2004). Chemical modifications improve the mechanical properties, filler dispersion, and thermal properties of composites (Chun *et al.* 2012, 2013a, b; Mohamad Rasidi *et. al* 2014).

The main goal of this research was to study the effects of PKS and its chemical modification on the tensile, morphological, and thermal properties of PLA/PKS biocomposite films. Surface modification using butyl methacrylate (BMA) was the chemical modification used to improve the tensile and thermal properties of PLA/PKS biocomposite films. The combination of PKS and PLA also offers an answer for maintaining the sustainable development of economical and ecological technology.

EXPERIMENTAL

Materials

Polylactic acid (PLA) was used as the polmer matrix and was supplied by TT Biotechnologies Sdn. Bhd., Pulau Pinang, Malaysia. The palm kernel shell (PKS) fibre was supplied by a palm oil manufacturer in Pulan Pinang, Malaysia. The PKS supplied was in powder form. The PKS were ground into fine powder and passed through a 63 µm sieve. The PKS fine powder was dried to remove excess moisture for 24 h at 80 °C. The average particle size of PKS powder was 63 µm, as measured by a Malvern particle size analyzer (Worcestershire, UK). Butyl methacrylate (BMA) was obtained from Merck Schuchardt OHG (Hohenbrunn, Germany), and ethanol was obtained from HmbG Chemical (Shah Alam, Malaysia). Both chemicals were in liquid form.

Chemical Modification

Butyl methacrylate was diluted to a 3% solution in ethanol. The PKS was added gradually to the BMA to ensure uniform distribution. The solution was then stirred at 500 rpm for 2 h. The treated PKS was dried for 24 h at 80 °C to remove excess ethanol.

Preparation of Biocomposite Films

PLA/PKS biocomposite films were prepared using the solution casting method.

A water bath set at 50 °C was used in this study. The PLA was dissolved using chloroform and stirred at 600 rpm for 20 min. After the PLA was completely dissolved, the PKS was gradually added to the PLA solution. The solution was stirred for 20 min. The solution containing PKS was cast into a petri dish and dried for 24 h to let the chloroform evaporate under room temperature. The obtained PLA/PKS biocomposite films were cut to dimensions of 25 mm × 100 mm for tensile testing. A similar procedure was conducted for treated PLA/PKS biocomposite films. Table 1 shows the formulation on untreated and treated PLA/PKS biocomposite films.

Table 1. Formulation of Untreated and Treated PLA/PKS Biocomposite Films

Materials	Untreated PLA/PKS Biocomposite Films	Treated PLA/PKS Biocomposite Films
Polylactic acid (php)	100	100
Palm kernel shell (php)	0, 5, 10, 15, 20	0, 5, 10, 15, 20
Butyl methacrylate*	-	3

php, part per hundred polymer; *3% from weight of PKS

Tensile Test

The tensile test was conducted in accordance with ASTM D638 (2014) using an Instron machine model 5569 (Grove City, USA). A gauge length of 50 mm was used, with a cross head speed of 10 mm/min. The test was performed at 25 ± 3 °C. The failure of the sample and load-elongation curve was obtained from the force that been applied. The tensile test was measured using 10 identical samples with dimensions of 25 mm × 100 mm for each biocomposite film.

The average values were reported. The tensile strength, elongation at break, and modulus of elasticity were obtained and calculated automatically using Instron proprietary software.

Morphology Study

The morphological study of PLA/PKS biocomposite films was carried out using a scanning electron microscope (SEM) (JEOL model JSM-6460LA, Tokyo, Japan) at 10 kV and 400x magnification. The fracture surfaces from the tensile tests of the specimens were mounted on aluminium stubs and sputter coated with a thin layer of palladium to avoid electrostatic charging during examination.

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Fourier Transmission Infrared (FTIR) analysis was used to characterize the presence of the functional chemical group in untreated and treated PLA/PKS biocomposite films. FTIR spectra of PLA/PKS biocomposite films were carried out in a Perkin Elmer Spectrometer 1600 series. The KBr technique was applied with the scanned range of 650 to 4000 cm^{-1}.

Thermal Gravimetric Analysis (TGA)

Thermal gravimetry analysis was used to examine the thermal degradation and thermal stability of the biocomposite films, using a Pyris Diamond Perkin Elmer Instruments (Q500, Massachusetts, USA) controlled by Pyris Diamond software. The scanned temperature range was from 30 to 650 °C, with a nitrogen flow of 50 mL/min and heating rate of 20 °C/min. The weights of the samples analyzed were 9 ± 10 mg.

RESULTS AND DISCUSSION

Tensile Properties

Figure 1 shows the effect of filler content on the tensile strength of untreated and treated biocomposite films. The tensile strength of the untreated biocomposite films decreased with an increase in filler content. The weak interfacial bonding between the PKS and the PLA matrix caused the tensile strength of the biocomposite films to decrease. The weak interfacial bonding was due to the hydrophobic nature of the PLA matrix, which only weakly binds to the hydrophilic surface (due to O-H groups) of the PKS. The different polarities in the bonding will not adhere with one another and led to failure under the applied force. Due to the weak interfacial adhesion, chemical modification of the PKS fibres was applied in this study. The treated PLA/PKS biocomposite films showed increasing values for tensile strength compared with untreated PLA/PKS biocomposite films. The average increment of tensile strength was 50% in the presence of BMA as a chemical modification. The chemical modification of the PKS fibre introduced good interfacial adhesion and dispersion in the PLA matrix.

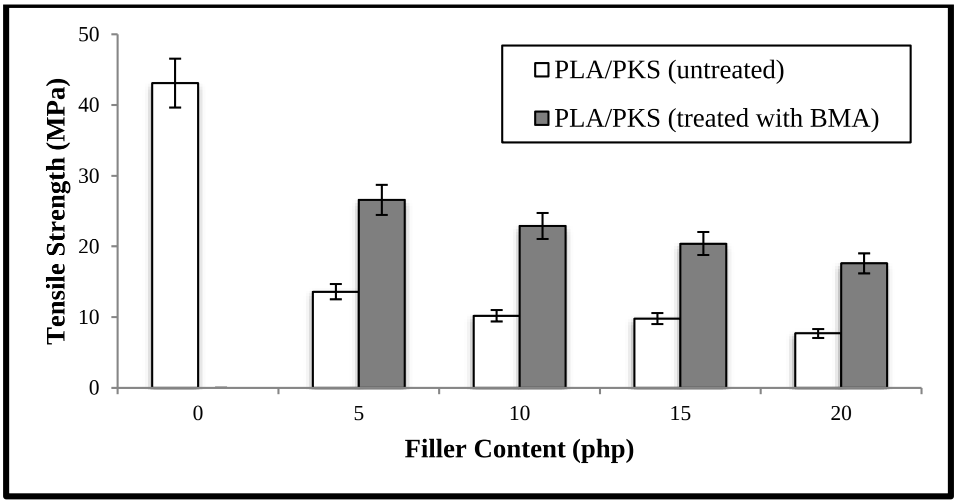

Fig. 1. Effect of filler content on the tensile strength of untreated and treated PLA/PKS biocomposite films

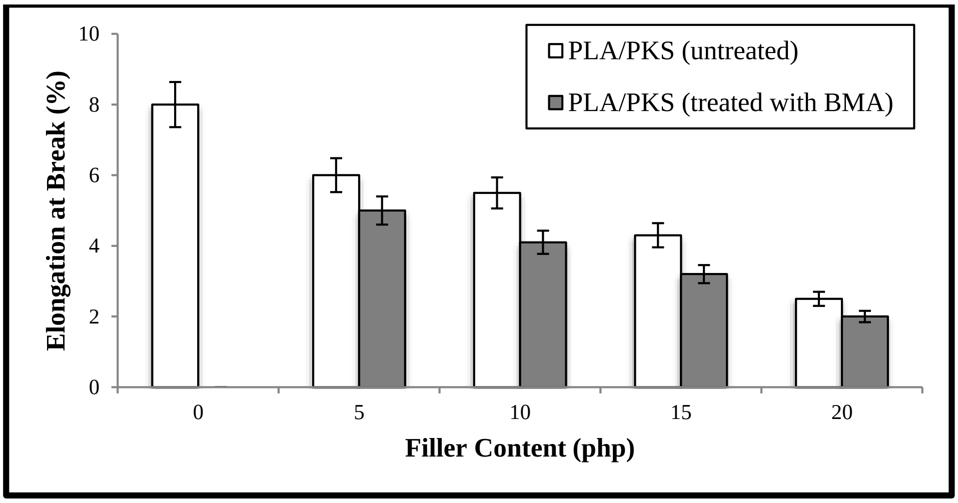

Fig. 2. Effect of filler content on the elongation at break of untreated and treated PLA/PKS biocomposite films

Figure 2 illustrates the effect of filler content on the elongation at break of untreated and treated PLA/PKS biocomposite films. The value of elongation at break for both untreated and treated decreased with an increase in filler content. The decrease in elongation at break is due to the fact that the filler-matrix interaction is weaker than the filler-filler interaction. Addition of PKS to the PLA matrix hinders the elongation at break, and significant distortions occur inside the PLA matrix. Improvements in stiffness can be made *via* the chemical modification of PKS. This is demonstrated by the fact that the value of the elongation at break of the treated PLA/PKS biocomposites film was lower than in the untreated biocomposites film. The stiffness increased, thus enhancing the filler-matrix interaction. The effect of filler content on the modulus of elasticity of untreated and treated PLA/PKS biocomposite films is shown in Fig. 3. As the filler content increased, the modulus of elasticity increased for both untreated and treated biocomposite films. The increasing value of the modulus of elasticity for untreated PLA/PKS biocomposite films is the result of the addition of filler inside the matrix, which enhances the stiffness, thereby increasing the modulus of elasticity of the biocomposite films. The treated PKS showed a higher value for the modulus of elasticity, with an average increment of 200%. The treatment of the fibres overcame the problem resulting from the filler-matrix interaction, as shown by the increases in interfacial adhesion between the PKS and the PLA matrix.

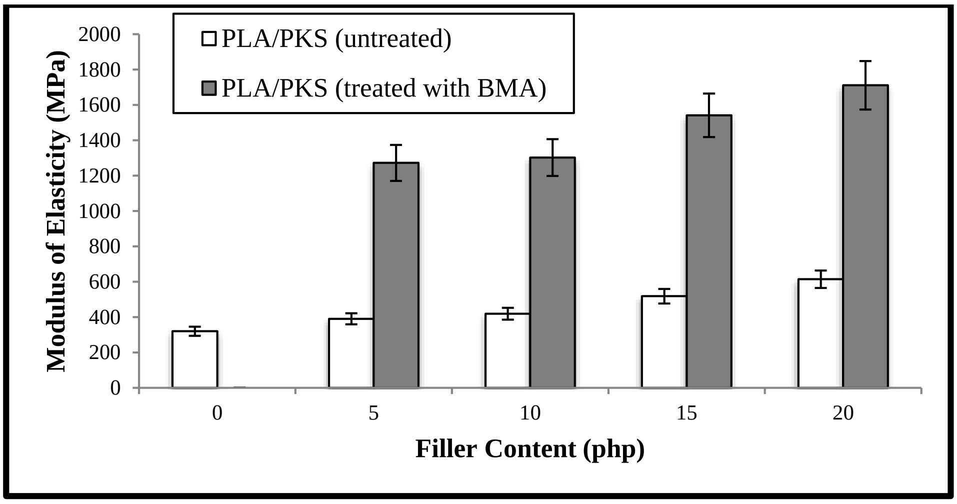

Fig. 3. Effect of filler content on the modulus of elasticity of untreated and treated PLA/PKS biocomposite films

Morphology Study

The micrographs of tensile fracture surfaces of PLA/PKS biocomposite films with a filler content of 10 php are illustrated in Fig. 4. The micrograph shows the rough fracture surface and the detachment of PKS from the PLA matrix. This indicated that poor bonding occurred between the PLA matrix and PKS. Moreover, the interaction and adhesion was also poor, which led to filler pullout and detachment of PKS. This result showed the lower tensile strength of the biocomposite films. Figure 5 shows the micrograph of the tensile fracture surfaces of treated PLA/PKS biocomposite films. A smooth fracture surface was observed with less filler pullout and agglomeration. This indicated good dispersion of filler throughout the matrix and good PKS wettability in the PLA matrix. The chemical modification of fibre using BMA resulted in better interfacial bonding and adhesion between the PKS and PLA matrix.

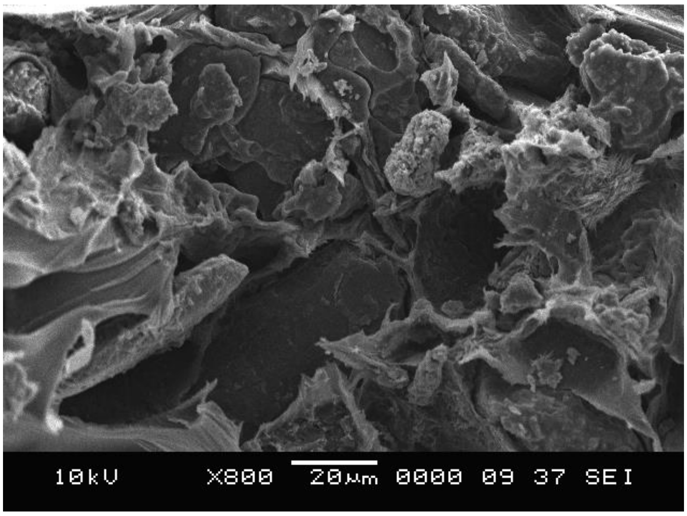

Fig. 4. SEM micrograph of untreated PLA/PKS biocomposite film (10 php PKS)

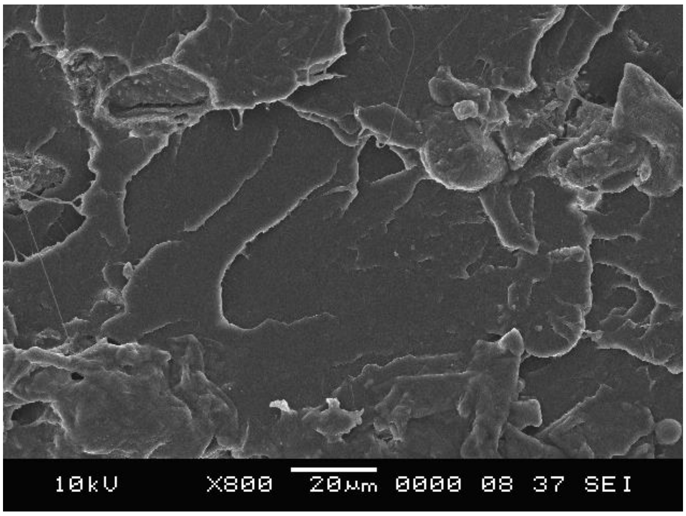

Fig. 5. SEM micrograph of treated PLA/PKS biocomposite film (10 php PKS)

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra of untreated specimens and those treated with BMA are shown in Fig. 6. Both plots contain a peak in the range of 3800 to 3000 cm^{-1}, indicating the presence of a hydrogen bond from the –OH group of the PKS filler. The peak at 1715 cm^{-1} indicated the C=O stretching of the carboxyl bond of the acetyl group from the hemicellulose components. The 1596 cm^{-1} indicated the conjugated C-O group for the aromatic skeletal in lignin, while the peak of 1466 cm^{-1} was attributed to the presence of C-H group in lignin and also peak from 700 to 880 cm^{-1} indicated the corresponding aromatic C-H group vibration in lignin. Moreover, the peak located at 1261 cm^{-1} was attributed to the presence of C-O group from acetyl group in lignin. The main components of cellulose and lignin was in the signal peak in the range of 1000 to 1150 cm^{-1} that included the C-O-C and C-O stretches. In the chemical modification of PKS, the adsorption of carboxyl group of BMA appeared at 1710 cm^{-1}, but the peak overlapping with carboxyl group belongs to PKS at the peak of 1715 cm^{-1}; thus it resulted in the peak shift to 1734 cm^{-1}. The intensity of the hydroxyl group (-OH) on treated PKS peak was reduced because of the hydroxyl group from PKS surface reacted with BMA via esterification as shown in Fig. 7.

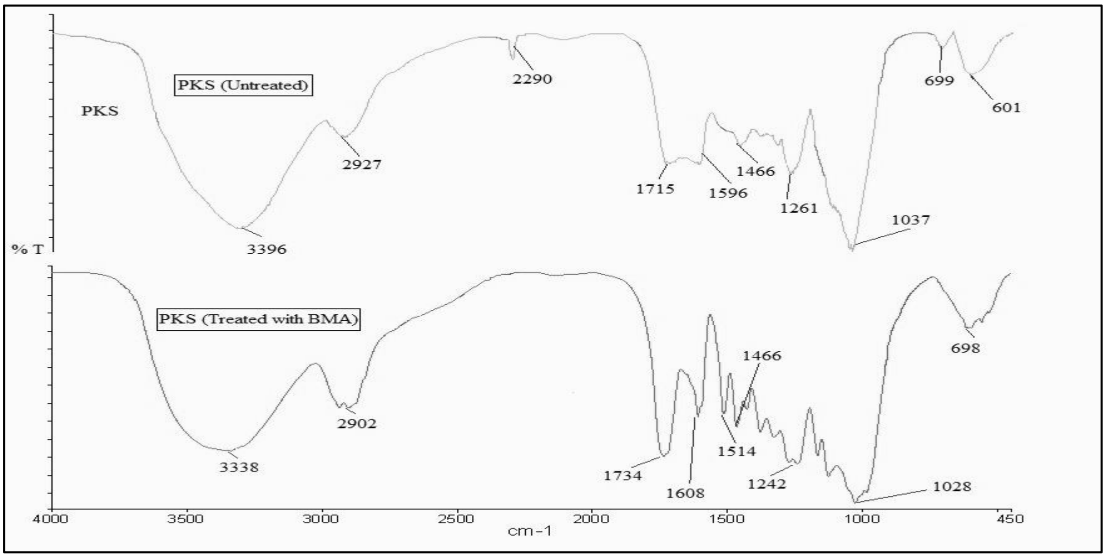

Fig. 6. FTIR spectra of untreated and treated PLA/PKS biocomposite films with BMA

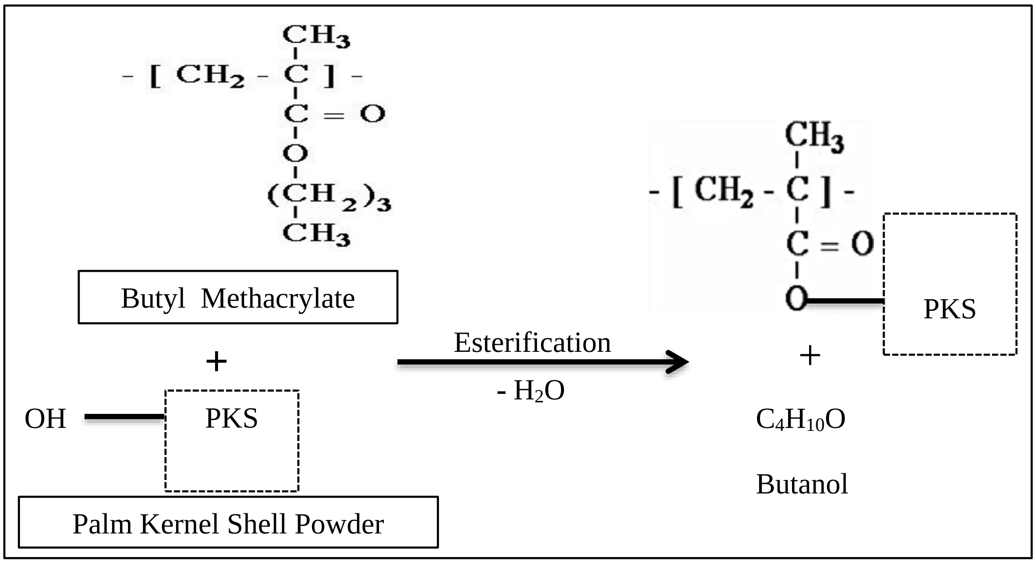

Fig. 7. Schematic reaction of PKS with BMA and PLA

Thermal Gravimetric Analysis (TGA)

Figures 8 and 9 show the TGA and DTG curves of neat PLA, PKS filler, and treated and untreated PLA/PKS biocomposite films with different filler contents. The total weight loss (T_{dmax}) at 300 °C and 600 °C of the neat PLA and treated and untreated PLA/PKS biocomposite films with different filler contents is summarized in Table 2. The DTG curve shows the decomposition trend of untreated PLA/PKS biocomposite films, similar to treated PLA/PKS biocomposite films. The T_{dmax} of untreated PLA/PKS biocomposite films increased with an increase in PKS content, but was lower than the T_{dmax} of neat PLA. The total weight loss of untreated biocomposite films at 300 °C increased with increases in PKS content but decreased at 600 °C. The residue of untreated biocomposite films increased with an increase in PKS content. At similar PKS contents, the T_{dmax} and residue of treated biocomposite films were higher than those of untreated biocomposite films. The total weight loss of treated biocomposite films was lower at 300 °C and 600 °C compared to untreated biocomposite films. This indicated that the treated biocomposite films had higher thermal stability than untreated biocomposite films. The positive effect of chemical modification using BMA is that higher thermal stability can be achieved due to better dispersion of PKS in the PLA matrix. Moreover, the stronger filler-matrix interaction improved the thermal stability of the treated PLA/PKS biocomposite films.

The DTG curves of Fig. 9 show the decomposition of PKS filler occur in two stages. In the first stage of degradation was in the temperature range of 230 °C to 300 °C in which the decomposition of hemicellulose occurred. The second stage entailed the decomposition of lignin and cellulose within the temperature range 300 °C to 450 °C. The treated and untreated PLA/PKS biocomposite films with BMA showed only one peak of degradation due to a shielding effect in which the PLA and PKS undergo decomposition at a similar temperature range. The treated PLA/PKS biocomposite films exhibited higher thermal stability compared to untreated PLA/PKS biocomposite films because they were fully decomposed at higher temperature. This is due to the improvement in interfacial adhesion and also better distribution of PKS inside the PLA matrix.

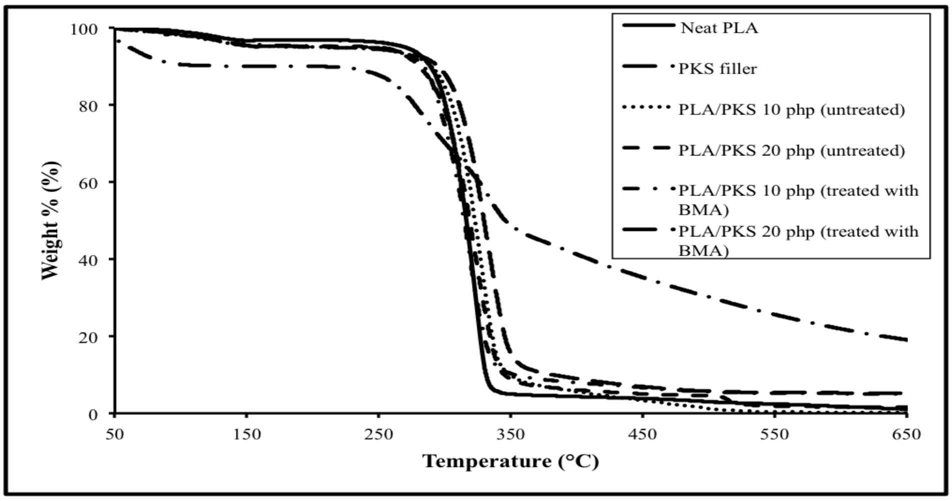

Fig. 8. TGA curve of neat PLA, and untreated and treated PLA/PKS biocomposite films

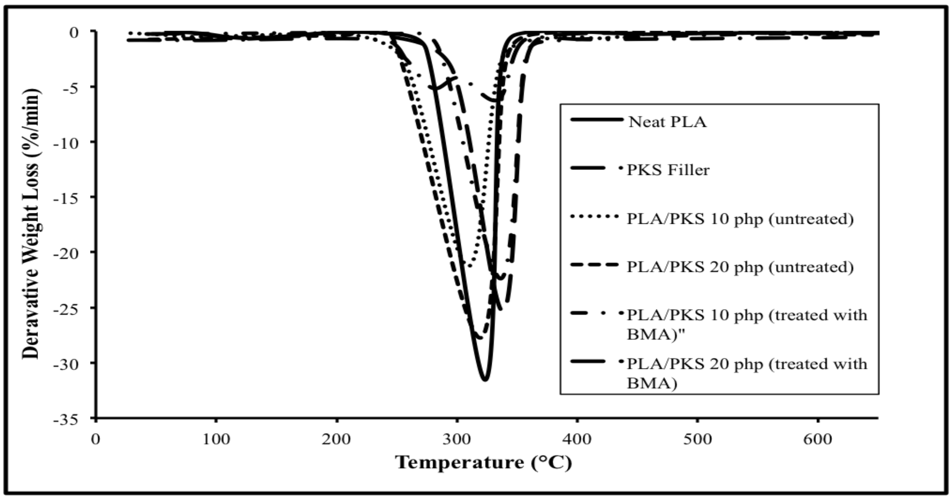

Fig. 9. DTG curve of neat PLA, and untreated and treated PLA/PKS biocomposite films

Table 2. TGA Data of Untreated and Treated PLA/PKS Biocomposite Films

Biocomposite Films	T_{dmax} (°C)	Total Weight Loss (%)		Residues
		300 °C	600 °C	
Neat PLA	323.8	3.1	100	0
PKS filler	334.8	10	81.1	18.9
PLA/PKS 10% (untreated)	309.3	9.2	99.9	0.1
PLA/PKS 20% (untreated)	318.7	10.6	97.5	2.5
PLA/PKS 10% (treated with BMA)	333.5	4.1	95.8	4.2
PLA/PKS 20% (treated with BMA)	337.2	6.3	93.9	6.1

- T_{dmax}: Degradation temperature at maximum

CONCLUSIONS

1. The tensile test showed that the addition of oil palm kernel shell (PKS) into the poly-(lactic acid) (PLA) matrix reduced tensile strength and elongation at break, but increased the modulus of elasticity of the biocomposite films. The treatment of PKS with butyl methacrylate (BMA) improved the value of tensile properties, such that the value of tensile strength and modulus of elasticity of treated biocomposite films was higher compared with untreated PKS.
2. The morphological study also indicated a poor interfacial adhesion between the untreated PKS and PLA matrix. The chemical modification using BMA improved the interfacial interaction between PKS and the PLA matrix, which improved the wettability of PKS fibres within the PLA matrix.
3. The treated PLA/PKS biocomposite films had better thermal stability compared with untreated PLA/PKS biocomposite films. The higher residue presence for treated biocomposite films indicated a better thermal stability due to good interfacial interaction and interfacial bonding between the PKS and PLA matrix under the presence of BMA.

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