

Improving Poly(Lactic acid) Properties by Using Fibre Reinforcement of Wild Silkworm *Attacus atlas*

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Abstract. Poly lactic acid (PLA) modification is needed to improve PLA properties. This can be done by adding natural fibre to the PLA matrix. This study aims to investigate both the thermal and mechanical properties of *Attacus atlas* fibre (cocoon and degummed fibre (DF)) and its biocomposites (PLA/*Attacus atlas* fibre). The thermal behaviour of *A. atlas* cocoon has a significant effect to heat treatment ($P < 0.05$) at 280, while DF at 240 based on colour change, weight loss, and fourier transform infrared (FTIR) spectroscopy which shows that *A. atlas* fibre can withstand temperatures of 180-200. The mechanical and thermal properties of the biocomposites of PLA/*Attacus atlas* fibre were investigated using tensile strength, tensile modulus, thermal strength, and FTIR. The *A. atlas* fibre weight both DF and non-degummed fibre (NDF) content of 5, 10 and 15 wt% was observed in PLA matrix. The addition of 5 degummed fibre (5% DF) to PLA increased the pure PLA tensile strength by 8% and produced the highest tensile modulus (2.24 GPa). The data indicated that the addition of PLA/5% DF will improve the mechanical properties of PLA. The addition of *A. atlas* fibre to the PLA changes the thermal character of the PLA, characterised by crystallinity degree changes.

Keywords: *Attacus atlas*, mechanical properties, thermal properties, tensile strength, tensile modulus

Introduction

Plastics are widely used and dominate almost all human needs including packaging (38%), building and construction (21%), automotive (7%), electrical equipment (6%), and other needs (28%) (European Commission, 2011). However, the dominance of high plastic demand has a serious impact on the environment. Plastic comes from non-renewable materials (petroleum) and causes problems through the accumulation of plastic waste that takes hundreds of years to degrade.

Poly lactic acid (PLA) is one of the alternatives to plastic-based materials that is categorised as an environment friendly polymer made of corn and it degrades naturally into humus, carbon dioxide, and water in a few weeks (Plackett and Sodergard, 2005). It could be used for food packaging based on EU Commission Regulation 10/2011, 14th January 2011 (Corbion, 2016). At present, PLA is one of the solutions to address the world's synthetic plastic problem. However, PLA needs modification to expand its use as

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a bioplastic. As such, the addition of natural fibres to the PLA may be of use. Natural fibres have excellent mechanical properties that could reinforce the properties of PLA. The addition of 20% kenaf fibre to PLA composites can increase the PLA's thermal strength from 69 to 120 °C and its flexural modulus from 4.5 GPa to 7.6 GPa (Plackett and Sodergard, 2005).

Attacus atlas fibre is a natural fibre synthesised from the *A. atlas* silkworm. This insect, also known as the wild silkworm, is found across almost all regions of Indonesia (Kundu *et al.*, 2012; Peigler, 1989). They are thriving due to the country's climate and its food sources. The conservation status of *A. atlas* is recorded as a non-endangered species (UNEP, 2017), so it is safe to use. This insect produces a large size cocoon, weighing 6.37 ± 1.07 g (Endrawati and Fuah, 2012) and thus its silk fibre is of great use and benefit.

Attacus atlas fibre consists of two proteins, namely fibroin and sericin. Fibroin is a protein fibre produced by the degumming process of the cocoon, to remove its sericin. Both DF and NDF have an excellent tensile

strength for composite materials; the tensile strength of NDF is 417-607 MPa, while the DF is 879-1689 MPa (Endrawati *et al.*, 2017). Their tensile strength is generally higher than cotton, jute, flax, ramie, or sisal fibres (Ku *et al.*, 2011) as well as *Bombyx mori* fibres (with and without sericin), collagen, tendon, and bone (Altman, 2003). The addition of the *A. atlas* fibre to the PLA matrix aims to reinforce the properties of and produce environment friendly composites. The result of this study is a new breakthrough for the use of new material from wild silkworm fibres in biocomposites.

This study aims to investigate the mechanical and thermal properties of *A. atlas* fibre and biocomposites of PLA/*Attacus atlas* fibre. Fibre analysis is important to ensure that the fibre can withstand exposure to high temperatures (around 180 °C) during the biocomposite manufacturing process. The thermal properties of the fibre must be examined to achieve these critical temperatures during biocomposite processing. It is necessary to discover the thermal properties of the fibre so that there will be no degradation in quality at the time of handling and processing. Therefore, this is the initial stage that characterises this study.

Materials and Methods

Materials. Biocomposites contain two materials that are the fibre and polymer matrix. Fibres were obtained from the *A. atlas* cocoon on a mahogany host plant in Imogiri, Special Region of Yogyakarta, Indonesia. The polymer matrix is PLA Purapol LX175 Corbion Purac.

Heat treatment of fibres. The samples used were the *Attacus atlas* cocoon (as NDF) and DF with the same range of colours, whitish brown (lightness (L) = 58.482.00, red or green (a) = 9.400.42, and yellow or blue (b) = 17.450.45). The cocoon is a pupal casing, which is a bunch of silk fibres, while DF refers to the degummed fibre extracted from the cocoon. Degumming starts by putting the cocoon, as much as 0.01 g/mL, into a solution (distilled water and 0.25N NaOH with a ratio of 2:1), and then fed into an autoclave Tommy High-Pressure Steam Steriliser ES-315 at 129 °C for 70.36 min (Endrawati, 2012). Then the cocoon and DF are put through heat treatments using a Nabertherm furnace 30-3000 °C at 100-320 °C for 30 min at each temperature level. The characterisation for the heat treatment consists of 1) colour change (ΔE) (a Colour Reader CR-10 Konika Minolta Sensing Inc. Japan was

used for this (Konika Minolta, 2017), (2) weight loss (%), and (3) Fourier transform infrared spectroscopy (FTIR) using a Fourier Transform Infrared Bruker Tensor 37.

Colour change is used to detect fibre changes before heat treatment and after heat treatment. In the colour reader, the value just appears as L (lightness), a (red/green), and b (yellow/blue). Therefore, to know the colour lightness difference (ΔL), difference of red/green (Δa), and difference of yellow/blue (Δb), data must be collected before treatment and symbolised as L₀, a₀, and b₀ and after treatment and symbolised as L₁, a₁, and b₁. The colour change formulation can be calculated by equation 1:

$$\text{Colour change } (\Delta E) = \sqrt{[(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]} \dots 1$$

where:

(ΔL) = the colour lightness difference (L₀-L₁); (Δa) = the value of the red or green difference (a₀-a₁), and (Δb) = the value of the yellow or blue difference (b₀-b₁).

The weight loss is the difference in weight before and after the heat treatment. The weight loss formulation can be calculated by equation 2:

$$\text{Weight loss } (\%) = \frac{w_0 - w_t}{w_0} \times 100 \dots\dots\dots 2$$

where:

W₀ = the non-treated fibre weight and w_t = the fibre weight at a certain temperature treatment.

Preparation of biocomposite processing. The biocomposites consist of two components, a fibre and a polymer. This study used NDF and DF *Attacus atlas* as a fibre and PLA as a polymer. PLA must be treated first at 100 °C for four hours before mixing with the fibre (Corbion, 2016). NDF has a length of 4.22 ± 1.65 mm and a diameter of 20.93 μm, while DF has a length of 4.22 ± 1.52 mm and a diameter of 20.95 μm (Fig. 1). NDF is derived from the cocoon that is treated mechanically without solvent chemicals, while DF is derived from degumming by combining mechanical and chemical treatment, like the DF sample in heat treatment. Fibre samples (NDF or DF) have a mixing ratio to PLA of 5, 10 and 15% (wt fibre to PLA). The biocomposites of NDF to PLA are called PLA/NDF, while the biocomposites of DF to PLA are called PLA/DF.

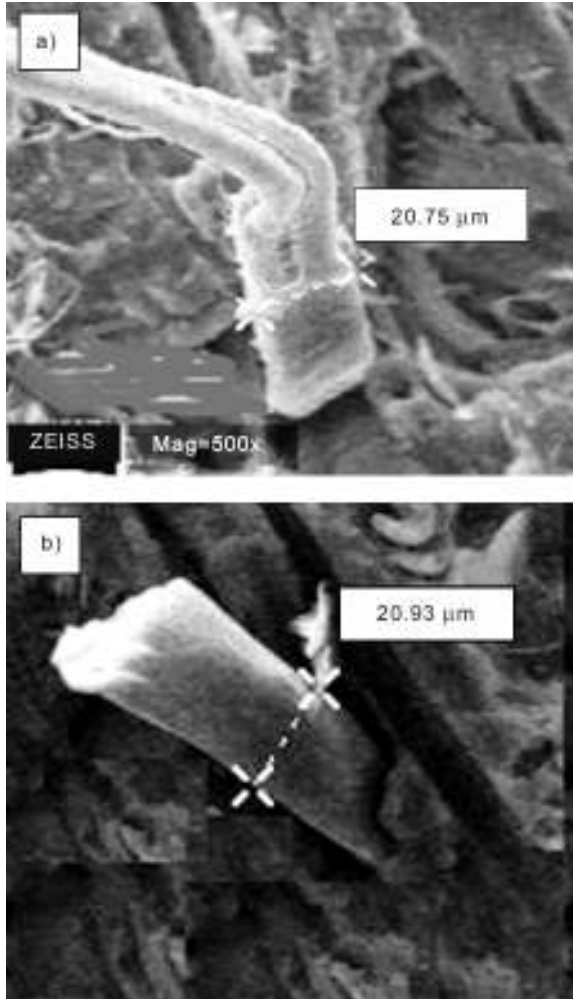


Fig. 1. Diameter of non-degummed fibre (NDF) (a), and degummed fibre (DF) (b) *Attacus atlas*. (Magnification 500×)

The biocomposite process consists of two stages, mixing and moulding. A Thermo Haake Polydrive was used in the mixing process at 180 °C in all extruder zones with a mixing speed of 100 rpm for 10 min. The mixing results were split into small pieces to simplify the moulding process. The moulding process consisted of three stages, first, melting for 4-5 min; second, pressing for one minute; and third, cooling for five minutes at 180 °C. Biocomposites were moulded with a density of 1 mg/ mm³, 1 mm thick, 60 mm long, and 50 mm wide (ASTM, 2016).

The characterisation for the biocomposites consist of mechanical and physical properties, FTIR spectral and Scanning Electron Microscope (SEM).

1. The mechanical characterisation was conducted according to the ASTM D638 standard with the Universal Testing Mechanical Shimadzu AG-IS 50kN (Fig. 2). The tensile strength was tested using a load cell of 1 kN at a tensile speed of 2 mm/s.

2. To characterise the thermal properties, a Differential Scanning Calorimetry (DSC) 4000 Perkin Elmer was used to measure the melting temperature (T_m), the crystallinity temperature (T_c), melting point enthalpy (ΔH_m), and the crystallinity degree (X_c) by equation 3. There were four processes in the DSC. First, the temperature was kept at 25 for 2 min. Then, the heating was carried out at 25-300 °C with a speed of 10 °C/min. Next, the temperature was kept at 300 °C for two minutes. Finally, the cooling was done at 300-25 °C with a speed of 10 °C/min. The result is displayed in the thermogram in the form of T_c, T_m, and ΔH_m.

The degree of crystallinity (X_c) was calculated according to Yong *et al.* (2010); Sha *et al.* (2009); Hoi *et al.* (2008) and can be obtained by:

$$X_c\% = \frac{\Delta H_m}{93.1} \times 100 \dots\dots\dots 3$$

where:

ΔH_m = the melting point enthalpy and 93.1 = the melting point enthalpy of 100% crystallinity.

3. For FTIR analysis, a Bruker Tensor 37 was used to determine the effect of heat treatments on the fibre and to detect the interface bonds between the fibres and the PLA matrix in biocomposites. The sample (biocomposite) in form of a pellet was made using a mini hand press. The pellet's composition was 200 mg KBr and 2 mg biocomposite that was homogenised using a mortar. The pellet was put into the FTIR device in the range of wavenumbers 400-3500/cm. The sample of infrared absorption was displayed in the form of wavenumber spectra at cm⁻¹.

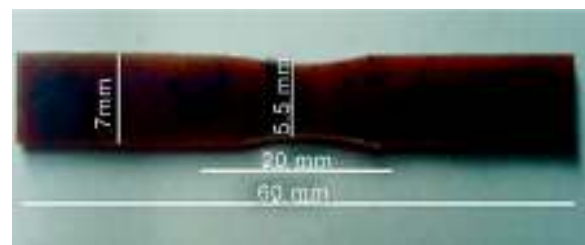


Fig. 2. Sample dimentions of PLA/*Attacus atlas* fibre biocomposite.

4. SEM analysis using a Carl Zeiss Bruker EVO MA10 was performed to see the morphology of the biocomposite fracture due to the tensile test so that the bond between fibre and PLA matrix could be clearly seen. SEM analysis began with the coating of a biocomposite sample with gold on a copper template prior to its inclusion in the SEM device. The gold layer served as a conductive coating to enhance the picture image produced by the SEM.

Data analysis. Data on heat treatment (colour change and weight loss) and biocomposites (mechanical and thermal properties) were analysed by ANOVA with completely randomised design.

Results and Discussion

Thermal properties of *Attacus atlas* cocoon. The material resistance of heat could be seen from changes in the fibre colour (ΔE), percentage weight loss, and FTIR spectra wavenumbers. *Attacus atlas* cocoons have a grey colour ($L = 57.83 \pm 2.82$, $a = 9.50 \pm 0.97$, and $b = 17.30 \pm 1.61$) before treatment. It did not change in colour up to 200 °C of heat treatment but there was a significant change to reddish brown at 240 °C ($P < 0.05$) with a colour change of 6.75 ± 0.44 (Fig. 3). The cocoon started turning dark brown ($\Delta E = 27.08 \pm 1.73$) at 280 °C and started to get black at 320 °C. The rate of browning increased (as a colour change to brown) depending on the temperature and water activities (a_w) (Nursten, 2005). The bound water decreased as the temperature increased and lead-free volume mobility was reduced. The bound water was completely removed at glass temperature (T_g). *Bombyx mori* fibre has a T_g of 178 °C (Hu *et al.*, 2007), while tussah fibroin has T_g of 190 °C (Freddi *et al.*, 1997). This aligns with the results in Fig. 3; under 200 °C there would not be any significant colour change because the browning process went slowly, while above 200 °C there was a significant colour change and percentage of weight loss (Fig. 3; Table 1).

Colour change was followed by an increase in weight loss (Fig. 3). Weight loss changed significantly above T_g because some intermolecular bound water evaporated. Heat treatment between 250 up to 350 °C revealed a chemical transition of fibre and produced new aromatic compounds at 350 °C (Se *et al.*, 2015). This condition could deliver increasing weight loss. At 320 °C, the cocoon began to darken and it corresponded with the cocoon decomposition temperature. *Bombyx mori*

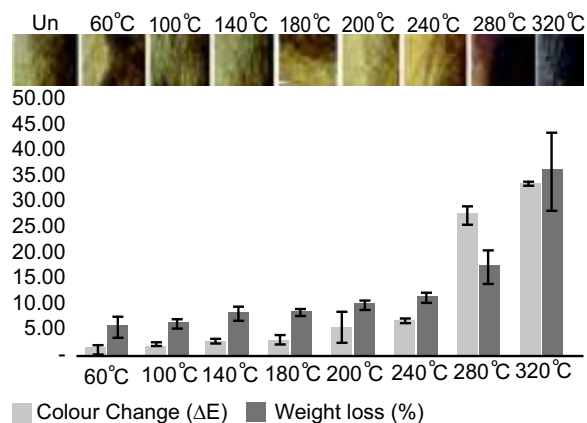


Fig. 3. Colour change and weight loss of *Attacus atlas* cocoon in heat treatments. Un=untreatment.

Table 1. Colour change and weight loss percentage of *Attacus atlas* cocoon

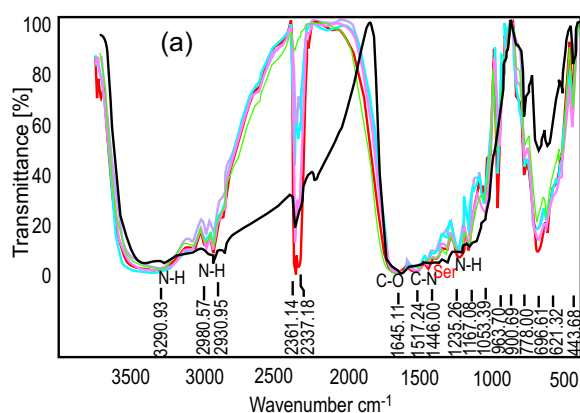
Heat treatment (°C)	Colour changes (ΔE)	Weight loss (%)
60	1.06±0.84 ^c	5.54±1.83 ^c
100	1.94±0.31 ^{bc}	6.19±0.75 ^c
140	2.66±0.47 ^{bc}	8.10±1.27 ^c
180	2.89±0.90 ^{bc}	8.30±0.55 ^c
200	5.42±2.99 ^b	9.71±0.74 ^{bc}
240	6.75±0.44 ^b	11.16±0.91 ^{bc}
280	27.08±1.73 ^a	17.04±3.27 ^b
320	33.17±0.19 ^a	35.66±7.41 ^a

Means in the same column with different superscripts (a, b, c) differ significantly ($P < 0.05$).

reaches a decomposition temperature at 312 °C (Zhang *et al.*, 2002) and tussah silk fibroin at 353 °C (Freddi *et al.*, 1997). At this stage, amorphous regions were degraded greater than the beta sheet regions and produced significant weight loss.

The cocoon spectra could reinforce the result of the colour change and weight loss. The cocoon has a wavenumber of 3290.93 cm^{-1} N-H stretching, 1645.11 cm^{-1} C=O stretching α -helix, 1517.24 cm^{-1} C-N stretching, 1235.26 cm^{-1} N-H deformation vibration, 963.70 cm^{-1} and 696.61 cm^{-1} as beta sheet, and 621.32 cm^{-1} α -helix (Fig. 4a). Wavenumbers at 3250-3300 cm^{-1} are N-H stretching (Amide II), 1638-1646 cm^{-1} are α -helix C=O stretching (Amide I), 1450-1600 cm^{-1} are beta sheet (Amide II), 700 cm^{-1} are beta sheet, and 621-664 cm^{-1}

are α -helix (Gallagher, 2017; Hu *et al.*, 2006; Stuart, 2004; Freddi *et al.*, 1997). While the wave-numbers at 1620 cm^{-1} (C=O stretching Amide I), 1520 cm^{-1} (C-N stretching Amide II), 1230 cm^{-1} (N-H deformation vibration Amide III), and 3040 cm^{-1} N-H stretching are the polypeptide bond spectra (Se *et al.*, 2015). Heat treatment could change in the secondary structure of proteins (Fig. 4). Spectra $1641\text{--}1644\text{ cm}^{-1}$ C=O stretching (random coil) appears at up to $240\text{ }^{\circ}\text{C}$ and excess $280\text{ }^{\circ}\text{C}$ has spectra of $1630\text{--}1631\text{ cm}^{-1}$ (strong



Control —
Treatment: 180°C — 200°C — 240°C — 280°C — 320°C —

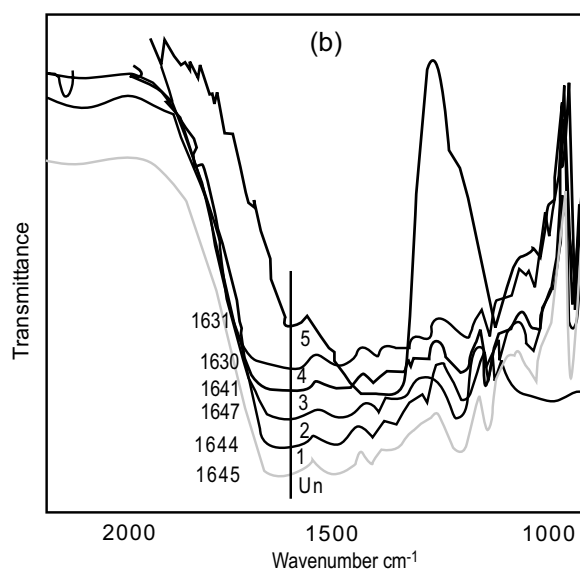


Fig. 4(a-b). Fourier transform infrared (FTIR) spectra of *Attacus atlas* cocoon, $500\text{--}3500\text{ cm}^{-1}$ (a), $1000\text{--}2000\text{ cm}^{-1}$ (b), untreated (Un), $180\text{ }^{\circ}\text{C}$ (1), $200\text{ }^{\circ}\text{C}$ (2), $240\text{ }^{\circ}\text{C}$ (3), $280\text{ }^{\circ}\text{C}$ (4), and $320\text{ }^{\circ}\text{C}$ (5).

intramolecular beta sheet) (Fig. 4b). The changes in the wavenumbers indicate a random coil transition to beta-sheet conformation. These results are consistent with Se *et al.* (2015) and exhibit clear characteristic peaks of beta-sheet conformation at heat treatment in excess of $280\text{ }^{\circ}\text{C}$.

The cocoon has heat resistant behaviour, first, water evaporated at around $100\text{ }^{\circ}\text{C}$ but the colour and weight loss did not change significantly; second, the suspected Tg was at around $200\text{ }^{\circ}\text{C}$; third, colour and weight loss changes (but not significant) began at around $240\text{ }^{\circ}\text{C}$ because there are no changes in the chemical structure (by FTIR spectra); and fourth, significant colour and weight loss changes, as well as a transition of random coil structure into beta-sheet, occurred at around $280\text{--}320\text{ }^{\circ}\text{C}$.

Thermal properties of DF. Degummed fibre (DF) is greyish brown ($L = 55.30 \pm 0.42$, $a = 10.20 \pm 0.71$, and $b = 16.85 \pm 0.35$). DF colour did not undergo a significant change in the heat treatment up to $200\text{ }^{\circ}\text{C}$ ($\Delta E = 1.02 \pm 0.48$) but it significantly changed at $280\text{ }^{\circ}\text{C}$. With this heat treatment, DF changed to a dark brown with $\Delta E = 28.81 \pm 3.03$ and weight loss changes of $21.40 \pm 4.04\%$ (Fig. 5). The significant colour changes in the DF corresponded with the percentage of weight loss. At the same level of heat treatment, DF has a colour change and weight loss greater than the cocoon. This might indicate that the chemical structure of DF changes faster than the cocoon. The cocoon has a sericin protein, which has a hydrophilic structure that will protect the

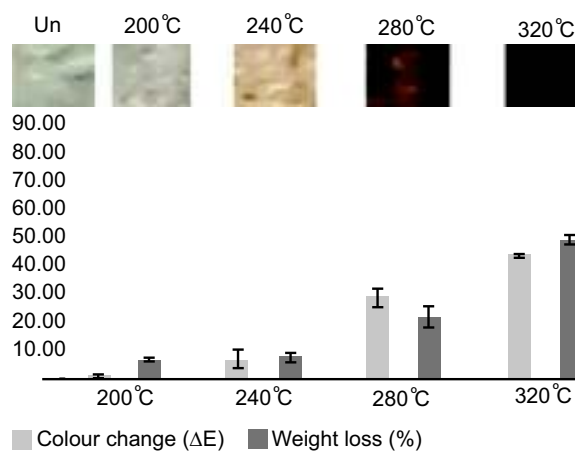
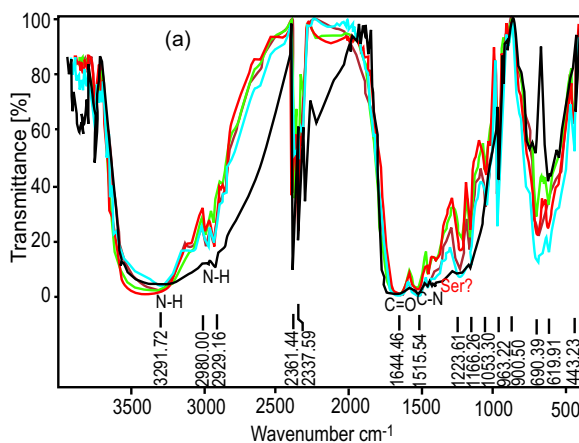


Fig. 5. Colour change and weight loss of *Attacus atlas* degummed fibre (DF) in heat treatments. Un = untreated.

fibroin from heat stress exposure, while DF does not have sericin because it was released during the degumming process. This is supported by the DF spectra; there was no serine amino acid absorption wavenumber and no sericin protein was indicated in the DF (Fig. 6a). Serine is the largest component of amino acids in sericin protein 28-29 (Mondal *et al.*, 2007) and has spectra wavenumbers at 1350-1250 cm^{-1} (Stuart, 2004).

Figure 6 shows the DF wavenumber before and after heat treatment. There are wavenumbers of 1644.46 cm^{-1} C = O stretching random coil (silk I) at spectra



Control —
Treatment: 200°C — 240°C — 280°C — 320°C —

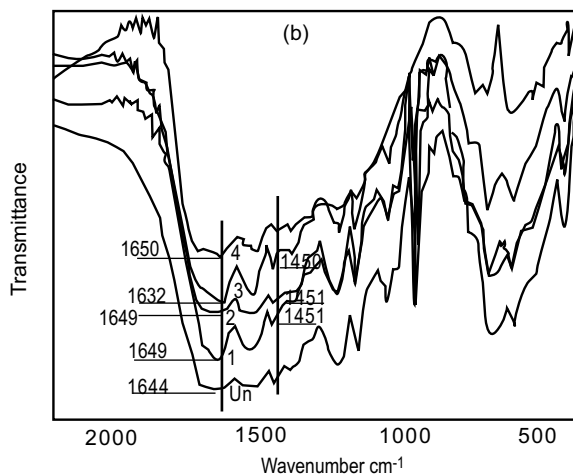


Fig. 6(a-b). Fourier transform infrared (FTIR) spectra of degummed fibre *Attacus atlas* (DF), 500-3500 cm^{-1} (a), 500-2000 cm^{-1} (b), Untreatment (Un), 200 °C (1), 240 °C (2), 280 °C (3), and 320 °C (4).

before heat treating the fibre and it has new absorption at 1451 cm^{-1} , which is an Amide II crystalline structure after heat treatment of 200-280 °C (Fig. 6b). The results indicate that a change of the beta sheet becomes stronger and increases the degree of crystallinity, the increase of which corresponds with the increase in heat treatment (Hu *et al.*, 2007). The wavenumber of 1450 cm^{-1} disappeared at the treatment of 320 °C. This is in line with the report by Se *et al.* (2015) where the beta sheet began to break down and transformed into sp²-hybridised hexagonal carbon at a temperature around 350 °C. This indicates that DF still has good thermal properties up to 280 °C.

Mechanical strength of biocomposite PLA/*Attacus atlas* fibre. The tensile strength of pure PLA was 56.24 ± 2.27 MPa, PLA/5% NDF was 59.62 ± 4.74 MPa, and PLA/5% DF was 60.74 ± 4.96 MPa. The addition of 5% DF to the PLA matrix increased the tensile strength by 8% compared with pure PLA, however, it decreased as the percentage of fibre increased (Table 2). The result was consistent with the prior study by Hoi *et al.* (2008); 5% tussah fibre in the PLA matrix produced the highest tensile strength that tends to decrease as the percentage of fibre increases. This condition indicates that the maximum fibre addition to PLA is 5%, more than that will cause a rise in viscosity decreasing the fibre distribution in the matrix.

In general, biocomposites of PLA/DF produced a greater tensile strength compared to PLA/NDF and pure PLA composite (Fig. 7). The biocomposite PLA/DF has a slightly higher ratio stress-stroke curve than others because DF makes up a crystalline region about 75% greater than an amorphous region of about 25%. The

Table 2. Tensile strength of PLA/*Attacus atlas* fibre biocomposite

Treatment	Tensile strength MPa	Tensile modulus GPa
Pure PLA	56.24±2.27 ^{ab}	2.23±0.04 ^{ab}
PLA/5%NDF	59.62±4.74 ^a	2.14±0.06 ^b
PLA/10%NDF	44.78±2.97 ^{bc}	2.33±0.18 ^{ab}
PLA/15%NDF	43.78±2.97 ^{bc}	2.38±0.24 ^{ab}
PLA/5%DF	60.74±4.96 ^a	2.24±0.12 ^{ab}
PLA/10%DF	55.77±6.64 ^{ab}	2.34±0.17 ^{ab}
PLA/15%DF	26.28±4.82 ^c	2.40±0.07 ^{ab}

NDF = non-degummed fibre; DF = degummed fibre. Means in the same column with different superscripts (a, b, c) differ significantly (P<0.05).

crystalline region contains repetitive amino acids (-Gly-Ala-Gly-Ala-Gly-Ser-), forming a beta sheet will be the most significant influence on the mechanical properties of the fibre. NDF still contains materials other than fibroin, such as sericin. The presence of sericin in the fibre produces a lower tensile strength than pure fibroin. The sericin contains an amorphous region greater than the crystalline region. The presence of sericin in fibroin decreases the single fibre strength from 610-690 MPa to 500 MPa (Yang and Bochu, 2009).

Interface bonding strength between DF and PLA is in line with the tensile strength of the biocomposite PLA/DF, which is greater than PLA/NDF. The strong interface bonding between the fibre and matrix caused an effective transfer of stress and load distribution through the interface and was ordered to improve the mechanical properties (Franco and Gonzales, 2005). These conditions can be seen in Fig. 8. The biocomposite of PLA/5% DF seems to have improved the interfacial bonding with the fibre having a shorter length compared to PLA/NDF interfacial bonding with extensive fibre pull-out. The strong interfacial bonding between matrix and fibres is characterised by the breaking of some microfibrils with a shear fracture of the composite (Ray and Rout, 2005). It is indicated that biocomposite PLA/5% DF has good interfacial bonding between the fibre and matrix.

The interfacial bonding in biocomposite PLA/5%DF was affected by the tensile modulus also (Table 2). That biocomposite has the highest tensile modulus (2.24 ± 0.12 GPa) that indicates a compact and strong composite.

Thermal properties of biocomposite PLA/*Attacus atlas* fibre. In this study, the melting temperature (T_m) of pure PLA is slightly higher (176.23 °C) than the data from the PLA Corbion (175 °C) by DSC analysis. Increasing the percentage of silk fibres in the PLA matrix did not significantly affect the changes to the T_m and T_c (Fig. 9). The T_g was not detectable in the thermogram because the crystalline structure was already formed on the biocomposite; this is supported by the increase in T_c . This is likely because the heating temperature (300 °C) is too high and damages the matrix, which then magnifies the damage by increasing the fibre percentage. This condition also causes the crystallinity degree to decrease in almost all treatments as fibre percentages increase.

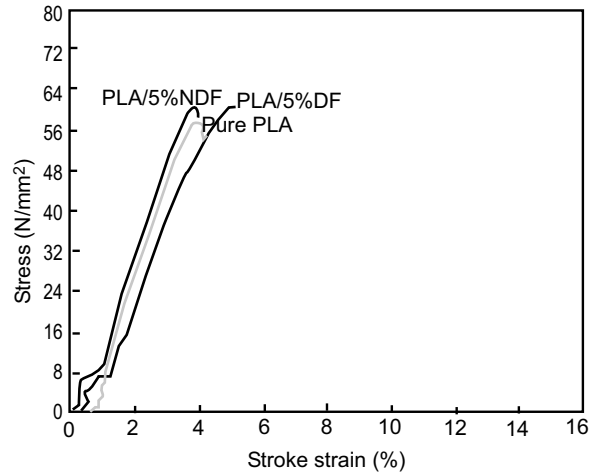


Fig. 7. Stress-strain curve of biocomposit PLA/*Attacus atlas* fibre.

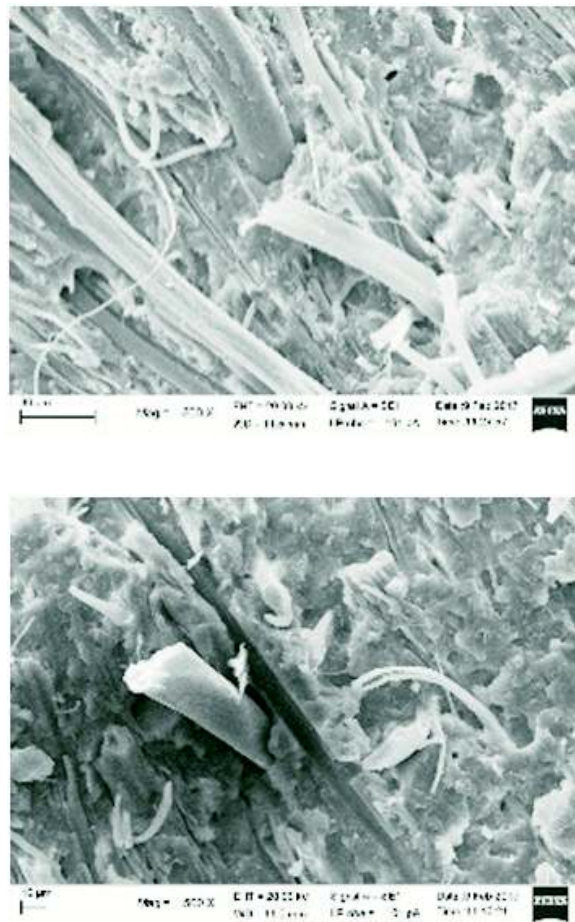


Fig. 8. Fibre fracture by scanning electron microscopy. Magnification 500X.

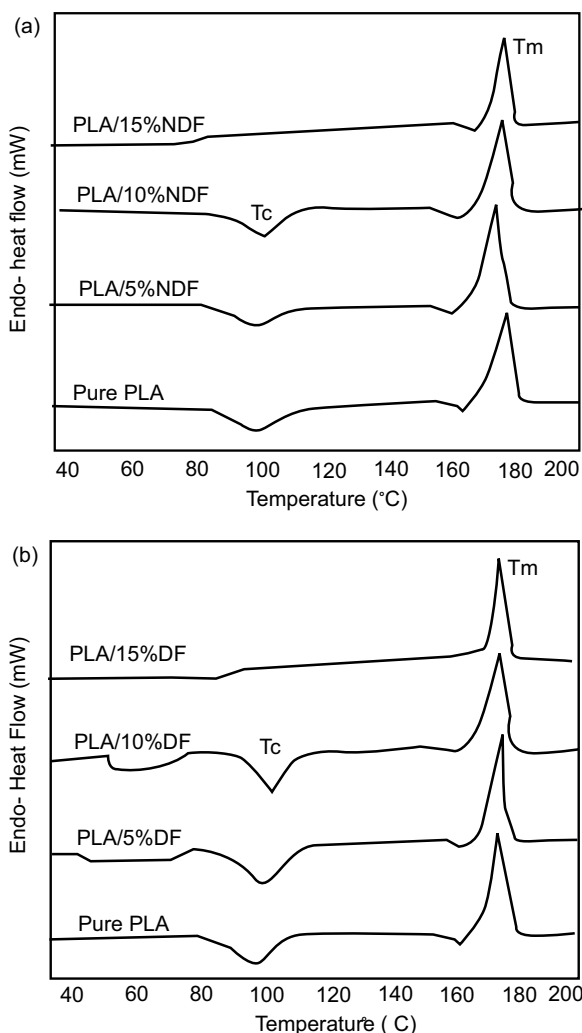


Fig. 9(a-b). Differential scanning calorimetry (DSC) thermogram of biocomposite non-degummed fibre *Attacus atlas* (PLA/DF) (a), and degummed fibre *Attacus atlas* (PLA/DF) (b).

The degree of crystallinity decreased as can be seen by the ΔH_m values, which tends to decrease as the percentage of fibres increase (Table 3). The ΔH_m value is the energy enthalpy used to melt per unit area of the biocomposite, so that if energy decreases, it may indicate that the crystallinity degree decreased. A decrease in the crystallinity degree may also indicate a decrease in mechanical strength.

FTIR spectrum of biocomposite PLA/*Attacus atlas* fibre. FTIR analysis can be used to determine the presence of new materials in biocomposites by looking at changes in the functional group. The pure PLA shows infrared absorption at wavenumbers 3503.01 cm^{-1} CH_3

Table 3. Physical properties of biocomposite *Attacus atlas* fibre to PLA matrix

Treatment	T _g	T _m	T _c	ΔH_c	ΔH_m	X _c
		(°C)		(J/g)		(%)
Pure PLA	ND	176.23	97.81	21.87	45.07	48.41
PLA/5%DF	ND	175.54	100.84	29.47	43.90	47.14
PLA/10%DF	ND	174.86	102.18	25.76	38.08	40.86
PLA/15%DF	ND	176.22	ND	ND	26.77	28.75
PLA/5%NDF	ND	174.56	98.98	16.29	43.03	46.22
PLA/10%NDF	ND	175.08	99.48	19.94	40.11	43.08
PLA/15%NDF	ND	177.03	ND	ND	46.05	48.39

Note: T_g and T_m collected from heating process; while T_c collected from cooling process; ND = not detectable.

stretching and 1746.97 cm^{-1} C = O stretching (Fig. 10). PLA has an infrared absorption spectrum at wavenumbers $100\text{-}3600 \text{ cm}^{-1}$, $3000\text{-}3500 \text{ cm}^{-1}$ CH_3 stretching, $1500\text{-}2000 \text{ cm}^{-1}$ C = O stretching, and $1000\text{-}1500 \text{ cm}^{-1}$ CC (O)-O stretching (Orozco *et al.*, 2009). The addition of 5% DF and NDF to the PLA matrix did not change the FTIR spectra, but in percentages of 10-15% DF and NDF, there was new infrared absorption at wavenumbers 1650 cm^{-1} and 1513 cm^{-1} (Fig. 10-11).

The wavenumber indicates that bonding between the fibre and matrix has happened. The infrared radiation from FTIR will be absorbed by molecules and cause the vibration of molecules. These vibrations are captured and displayed as absorption of wavenumbers by FTIR. If new wavenumbers appear in the biocomposite spectral and it is identical to the DF or NDF wavenumbers, it shows that a bond between DF or NDF with the matrix PLA has occurred.

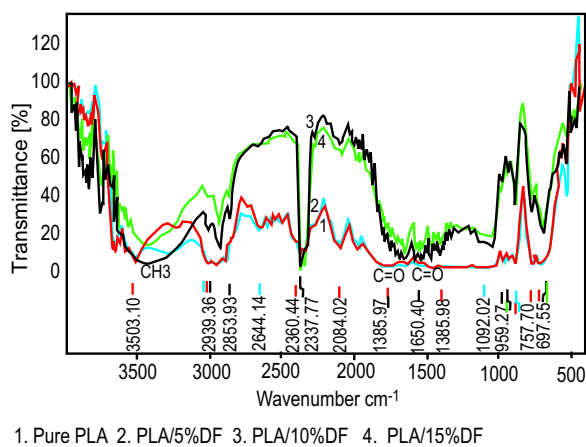
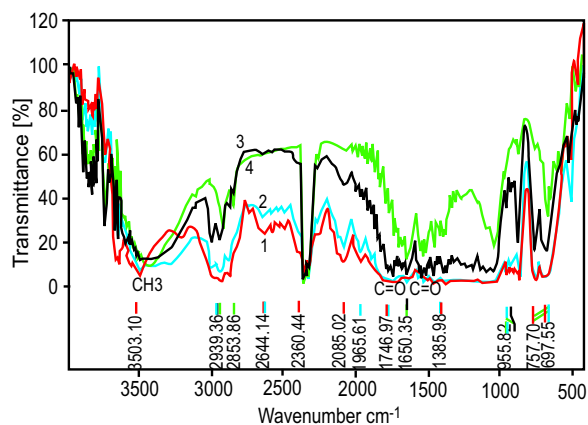


Fig. 10. FTIR spectra of biocomposite PLA/DF.



1. Pure PLA 2. PLA/5%NDF 3. PLA/10%NDF 4. PLA/15%NDF

Fig. 11. FTIR spectra of biocomposite PLA/NDF.

Conclusion

This study found the critical temperature for the use of cocoon and degummed fibre (DF) of *Attacus atlas* silkworm in Poly lactic acid (PLA). The *Attacus atlas* cocoon undergoes significant chemical changes at 280 °C heat treatments, while DF has significant chemical changes at 240 °C, which was analysed by weight loss, colour changes, and FTIR spectra. The thermal properties of *Attacus atlas* fibres will work well to create a composite at temperatures of 180-200 °C. During the study, difference percentages of *A. atlas* fibre were added to the PLA matrix: 5%, 10%, and 15% wt. The addition of 5% DF in the PLA matrix can increase the tensile strength by 8% to improve PLA's mechanical properties. The properties of PLA/5% DF are comparable to those of other natural fibres used in industrial polymeric composites.

In this study, it was found that sericin has an excellent role in fibre protection and this is evident from the higher cocoon heat resistance than that of DF. However, when it is combined with the PLA matrix, sericin will interfere with the bond between the fibre and the PLA matrix. This has an impact on the mechanical properties of smaller PLA/NDF than PLA/DF biocomposites.

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