Waste and Biomass Valorization
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ORIGINAL PAPER

Valorisation of Agricultural Residue Bio-Mass Date Palm Fibre in Dry-Blended Polycaprolactone (PCL) Bio-Composites for Sustainable Packaging Applications

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Abstract

Purpose This study experimentally developed and characterised dry-blended Polycaprolactone (PCL)/date palm fibre biodegradable composites for sustainable packaging applications. Date palm fibres are collected from date palm trees as by-products or waste materials. They will be valorised in bio-composite application to promote fibre-based sustainable packaging items over their non-biodegradable synthetic polymer based conventional packaging products. In the dry-blending process, fibre and polymer are mixed with a shear mixer, while, in a melt-blending process, an extruder is used to extrude fibre/polymer blends after applying heating and high shear pressure to melt and mix polymer with fibres. Dry-blending process offers many comparative advantages, such as less equipment, steps, cost, process degradation, energy consumption and hence, lower harmful environmental emissions; while, a proper fibre/polymer mixing is a challenge and it needs to be achieved properly in this process. Therefore, it is important to understand the effects of dry-blending process on manufacturing of PCL/date palm fibre bio-composites for packaging applications, before promoting the dry-blending as a suitable alternative to the melt-blending process.

Methods Short chopped fibres were grinded as powders and dry-blended at a ratio of $(0-10\%)$ (w/w) with PCL polymer using hand and a shear mixer for 30 min, following a compression moulding process to produce bio-composite samples. Tensile, water contact angle, SEM, TGA, DSC and DMA tests and analysis were conducted. The dry-blended PCL/date palm fibre composites' properties were compared with reported melt-blended samples' results found in literature.

Results Dry-blended samples showed an increase in tensile modulus values (up-to 20%) with fibre inclusion and these values were found close to the melt-blended samples in the literature. Tensile strength and strain values were reduced which could be related to the poor fibre/polymer interface. Fibre addition affected the thermal, thermo-mechanical and crystallisation processes in PCL polymer matrix.

Conclusion Dry-blending is capable of producing bio-composites with a very comparable properties to melt-blended counterparts, although a more details study is needed to conduct in future. The results of this study, could be used carefully to design dry-blended PCL/date palm fibre bio-composites for possible packaging applications. The irregular fibre distribution in dry-blended samples could be improved in different ways which should be investigated in future.

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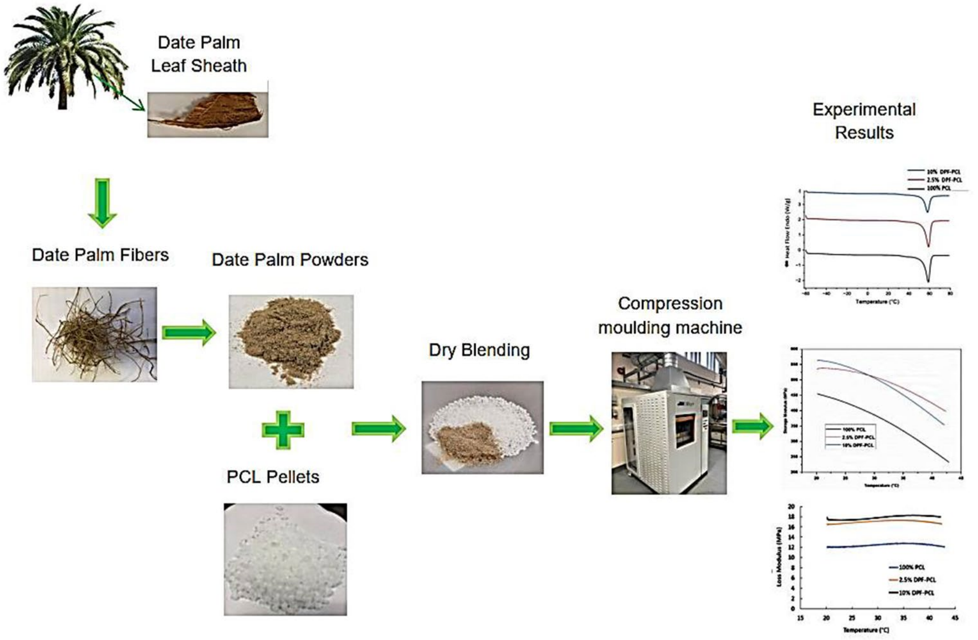
Graphical Abstract



Keywords Date palm fibre · Valorisation · Dry-blending · Melt-blending · Sustainable packaging · Polycaprolactone (PCL)

Introduction

Synthetic fibres are typically derived from petroleum-based sources, which contribute to negative environmental impact and deplete non-renewable resources. In contrast, natural fibres a competitive alternative, especially those derived from plants (flax, hemp, jute, date palm fibre), are renewable and biodegradable [1]. The processing of natural fibres has less impact on the environment compared to synthetic fibres [2]. Natural fibres may require a higher percentage in fibre reinforced composite applications compared to glass fibres, but this leads to a reduction in resin percentage, resulting in pollution reductions caused by non-biodegradable polymers [3]. The low density of natural fibres leads to better specific efficiency, resulting in fewer emissions during service life such as automotive applications [4]. Lower energy consumption in processing of natural fibre contributes to overall environmental sustainability and the natural fibres show superior environmental performance in various aspects when compared to synthetic fibres, such as glass fibres [3]. Natural fibres have additional advantages, including low cost, good thermal and acoustical insulation characteristics, energy recovery, reduced tool wear in machining operations, degradability, and reduced dermal and respiratory irritation. Despite these benefits, challenges hinder the widespread adoption of natural fibres in polymer matrix composites. High moisture absorption and poor adhesion present obstacles, limiting applications and requiring strategies such as coupling agents, fibre property enhancement through various chemical treatments, and careful production method selection [5]. Additionally, the irregularity in natural fibre shape poses difficulties in predicting mechanical properties.

Composite materials have evolved by incorporating synthetic fillers like carbon and glass fibres and into thermosets or thermoplastic polymer matrices such as epoxy, polyester, vinyl ester, polyethylene, polypropylene, polyethylene terephthalate and polyamide. Nevertheless, the increasing need for environmentally-friendly products has led to a transition towards the creation of composites produced from biological sources and are also capable of decomposing naturally [6]. Lignocellulosic fibres derived from plants have become increasingly popular as organic fillers in developing composites. These fillers are commonly combined with biodegradable polymer matrices like polylactic acid (PLA), thermoplastic starch (TPS) and polycaprolactone (PCL), which can be produced from biomass or synthesized from petroleum [7]. These materials have the qualities of being biodegradable and/or recyclable, and in numerous instances, they are completely produced from biological sources. Furthermore, these materials exhibit non-toxic characteristics, high tensile and flexural modulus, the ability to be processed at lower temperatures, and adjustable properties for specific uses.

The increasing awareness of the need to conserve non-renewable natural resources has led to the advancement of environmentally friendly applications of advanced polymeric materials, specifically bio-based composites derived from agricultural and industrial waste products. This movement corresponds to the wider transition towards sustainable practices, propelled by environmental concerns and efforts to mitigate climate change. Agro-industrial wastes, which are produced during agricultural processes, and by-products, which are generated from industrial activities, are acknowledged as inexpensive raw resources that have considerable promise to be valorised for the development of advanced sustainable materials. Various literature recognizes the economic and environmental benefits of using renewable sources, highlighting their ability to break down naturally and reduce waste [8]. Bio-based composites offer a viable alternative to conventional polymeric materials due to their renewable source and frequently biodegradable properties. This strategy not only helps conserve resources but also tackles concerns regarding trash disposal and environmental effect. While biopolymers possess renewability and biodegradability, they frequently demonstrate diminished mechanical strength, permeability, and thermal stability, restricting their applicability in certain contexts [9]. A prevalent approach to augment their overall performance and enhance commercial feasibility entails introducing reinforcing agents [10]. These additives, alternatively termed fillers or reinforcements, are integrated into biopolymers to enhance particular properties like strength, resilience, and thermal resistance. The potential of agricultural bio-waste as effective reinforcements in composite manufacture reported in various literatures [11]. Furthermore, bio-waste can be valorised and utilized in many formats to produce composite materials and their wide-ranging uses. The adaptability of bio-waste can be used at many stages and processes, leading to enhanced characteristics of composite materials.

Date palm fibres are sourced from date palm trees, mainly cultivated in hot and humid regions, such as Arab and North African countries. Although date palm trees are cultivated mainly for fruits, date palm fibres are collected as by-products or agricultural waste materials from yearly fruit harvesting activities, or maintenance and pruning actions of these tress to encourage their good growth. The production of date palm fruit on a global scale has consistently shown a steady increase, highlighting the growing significance of date palm trees. It is estimated that currently near about 100 million date palm trees are present worldwide [18]. A single date palm tree produces at-least 26 Kg/year of agricultural waste materials from different parts of its structure [12, 13] and from this, it can be easily understood the amount and availability of date palm fibre agricultural waste bio-mass across the world. It has been reported that only in MENA (Middle east and North Africa) regions, this agricultural waste materials production can be varied from 2.6 to 2.8 million tonnes annually [12].

Presently, a significant portion of date palm fibres is directed towards low-value products. Thus, finding sensible and innovative methods to utilize agricultural residues like date palm fibres is gaining attention from both researchers and industry. The goal is to move away from traditional low-value applications and explore new ways of incorporating these fibres into polymer composite reinforcements or other advanced applications, which could lead to enhanced resource utilization and value creation. This approach not only aligns with sustainability goals but also has the potential to offer economic benefits. Various research has been carried out using recyclable or virgin thermoplastics like High Density Polyethylene (HDPE) and polypropylene (PP) with virgin or recycled natural fibres [14] with keeping the sustainability goal in mind. Date palm wood flour mixed with recycled polypropylene exhibited increased tensile strength [15] and similar results are reported by reinforcing recycled high density polyethylene with date palm fillers [16].

Date palm fibres can be turned into as foam materials and utilised them for heat and sound insulation properties. Chemical blowing agents [17] can be mixed with fibres in a polymer matrix, which can be melted and create foaming bubbles in mixed fibre-polymer phases during the manufacturing process of fibre/polymer-based foam. For date palm fibre in polymer composites, Mousa et al. reported the date palm agricultural biomass mixed with PLA using melt blending technique showed higher elongation at break with the addition of plasticizer and shows potential in semi-structural packaging applications [18]. Films of PLA reinforced with date palm leaves fillers manufactured using extrusion blowing techniques are also reported to show enhanced tensile properties [19]. The incorporation of date palm midrib powder as a reinforcing filler in the biodegradable polyvinyl alcohol (PVA) matrix led to a significant improvement in tensile strength [20]. Dhakal and co-authors [21] studied the mechanical properties of date palm fibre leaf sheath powders with biodegradable polycaprolactone (PCL) as matrix and reported that the tensile strength is highest at 20%wt and is comparable with other agricultural waste biomass like wheat bran [22]. Dhakal et al. further reported that using PCL as a matrix in date palm composites in comparison with other polymers like TPU, PLA and phenolic resin showed higher tensile strength and the plausible explanation of this is higher affinity of PCL at the interface of the lignocellulose fibres.

Conventional packaging derived from petroleum is widely utilized in various applications owing to its notable features such as impressive specific strength, durability, ease of processing, and cost-effectiveness. However, despite these merits, this type of packaging comes with a substantial environmental downside as it requires several centuries to undergo complete decomposition [23]. The protracted decomposition period gives rise to significant environmental concerns, creating difficulties in waste management and sustainability efforts. Natural fibre based sustainable packaging are gaining upmost importance in the recent time in order to limit the production of conventional petroleum-based packaging materials. Utilizing composite materials composed of natural fibres is highly advantageous in packaging applications, particularly as an alternative to synthetic materials derived from petroleum. A noteworthy example is - a company specializing in packaging material crafted from coconut fibre, and there are several attempts being made to produce food packaging utilizing cereal waste, such as straw [24, 25]. The utilization of date palm fibres and agricultural waste biomass in powdered form presents a substantial merit as a filler material in food packaging. From an environmental perspective, these materials pose no complications in terms of recycling or disposal after use.

Polycaprolactone (PCL) is a potential fossil-based biodegradable material for sustainable packaging applications and its various properties such as hydrophobicity, moisture or oxygen barrier performances, mechanical properties etc. are engineered and tailored through blending with other bio-polymers, such as PLA [26]. PCL is reported to exhibit lower tensile strength but when blended with another biodegradable polymer PLA, showed higher stiffness. In this regard, valorisation of agricultural biomass (date palm fibres) as reinforcing agents in different bio-degradable polymers like PCL, has the potential to enhance the overall mechanical behaviour of fibre/polymer bio-composites for semi-structural or non-load bearing packaging applications [27]. There are two ways date palm fibres can be used in a polymer matrix – (1) for fibre reinforced composites, date palm fibres (long, short, chopped etc.) can be placed as layer by layer with polymer matrix, followed by a compression moulding or other fibre reinforced composite manufacturing technique and (2) fibres at a particular size can be blended with polymers and use this fibre/polymer blend in different plastic moulding processes, such as injection, compression etc. to produce ultimate products. The fibre/polymer blending process can be done in two different ways- (1) melt blending through an extrusion process and (2) dry-blending process.

In an extrusion melt blending process, heating and higher shear force are used to melt polymer, so that the melted polymer can be mixed with fibres properly. This is an established industrial process to mix fibres in the polymer effectively and properly. In contrast, an extrusion process requires expensive equipment, initial investment in any industry, highly skilled manpower to operate the equipment, large space to accommodate equipment and the whole manufacturing process and the most importantly, the extrusion process itself requires an extensive amount of energy consumption for material processing. In addition, it has been reported that in the melt blending process, date palm fibre/PP bio-composites face thermal degradation [17] which could be harmful for ultimate composites performances in a real-life environment. Unlike the melt extrusion process, in a dry-blending process, fibres are mixed with polymer by manually and/or with a high-speed shear mixer without applying any heating for the polymer melting. Although, a dry-blending is an easy process, requires no special equipment/initial business investment/significant fibre and polymer degradations, less process energy consumption and cost, this process has a lacking of proper fibre distribution in the polymer matrix. Considering the advantageous characteristics of a dry-blending process, it is possible to use the dry-blending as an alternative to the melt blending process and this needs an in-depth study on the performance analysis of any dry blended fibre/polymer bio-composites. The process optimisation and the removal of the extrusion process for the blending of fibre and polymers, will allow the cleaner production concept in this field, which will ultimately reduce process waste, energy and resource consumption for the manufacturing of bio-composites, promote workers safety work environment and a quicker process leading to a lower production cost.

In this work, we added date palm fibre in PCL polymer matrix through a dry-blending process and the dry-blended fibre-polymers were used in a compression moulding technique to manufacture PCL/date palm fibre bio-composites for sustainable packaging applications. PCL is a cheap, hydrophobic, fossil-based biodegradable polymer, abundantly available in the current market and low melting polymer which have made the bio-composite manufacturing process easier in terms of energy and resource consumption. Date palm fibres were grinded into powder so that they could be mixed in a better way with PCL polymer pellet during the dry-blending process. The objectives of this study were to develop dry-blended PCL/date palm fibre bio-degradable composites at different fibre/polymer weight ratios and characterise their mechanical, water contact angle, thermal and thermo-mechanical properties. Also, these properties of dry-blended bio-composites were compared with melt blended PCL/date palm fibre samples, reported in literature so far, in order to understand the effects of dry-blending on PCL/date palm fibre composites' properties so that they can be applied in sustainable packaging applications.

Table 1 Date palm fibre details

Fibres	Density (g/cm^3)	Breaking tensile strength (MPa)	Tensile modulus (GPa)	Elongation (%)
Date palm fibres	0.9–1.2 [1, 28, 29]	170–275 [1]	5–12 [1]	5–10 [1]

Materials and Methods

Materials

PCL polymer was purchased from Easy Composites, UK as the Mouldphorm grade with a molecular weight (M_w) of 55,000 g/mol, MFI of 9 g/10 min (80° C, 2.16 Kg) and density of 1.145 ($^{g}/_{cm^3}$). Leaf sheath date palm fibres were collected from Saudi Arabia (Al-Ahsa, Eastern Province) as long fibres in bundles. Date palm fibre physical and mechanical properties are given in Table 1 [1, 28, 29].

Date Palm Fibre Grinding Process

Long fibres were cleaned in hot water, dried in an open environment for 72 h, then chopped into 1 cm long fibres, followed by a further drying operation in an oven for two hours at 80 °C. The dried chopped fibres were grinded into powders using a powerful laboratory scale bench-top RETSCH Ultra Centrifugal Mill ZM 300 in a cryogenic grinding mode to avoid any fibre degradation during the grinding operation (Fig. 1). The grinding speed was up-to 18,000 rpm and a stainless-steel ring sieve of 350 µm was used to produce the fibre powder with a range of particle size of 350–500 µm. In this mill the grinding operation is happened by impact and shearing effects between the rotor and the fixed ring sieve (Fig. 1).

Table 2 PCL/date palm fibre bio-composite samples details

Samples	PCL (w/w %)	Date palm fibre powder (w/w %)
100% PCL	100	---
2.5% DPF-PCL	97.5	2.5
5% DPF-PCL	95	5
7.5% DPF-PCL	92.5	7.5
10% DPF-PCL	90	10

Dry-Blending and Compression Moulding for PCL/Date Palm Fibre Bio-Composite Manufacturing

Date palm fibre powders were blended with PCL polymer pellets at different ratios (Table 2) by the dry-blending process using hand mixing followed by a shear mixing process. The dry blended PCL/date palm fibre mixtures were compression moulded into 160 mm (l) × 160 mm (w) × 2 mm (t) moulded plaques using an electrically heated hydraulic press. The compression moulding process involved the heating of empty mould (both upper and lower parts of the mould) at 120° C for 20 min, the subsequent placing of polymer and fibre mixtures evenly on the lower part of the mould very quickly and closing the mould, followed by a heating stage of the mould with fibre/polymer mixture for 10 min at 120° C without any pressure. After that, a 5 MPa pressure was used on the mould for 8 min at the same temperature. with the following pressure release and normal air-cooling stages for the temperature down to 20° C before the de-moulding of moulded bio-composites was taken place.

Tensile Testing

Tensile test was conducted on PCL/date palm fibre bio-composite samples according to ISO 527 -2 test standard using a Universal testing equipment (Zwick/Roell Z010) with a load cell of 10 kN. ISO 527-2 5 A type test specimens were cut from moulded bio-composite panels with a cutting puncher and they were tested at a displacement rate of 50 mm/min

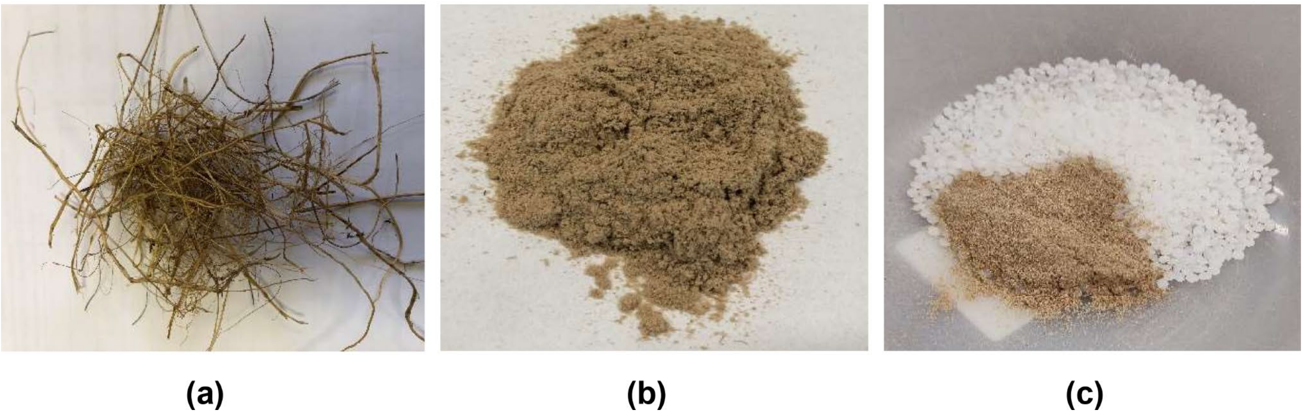


Fig. 1 Date palm fibres and PCL polymer pellets – (**a**) original long fibres, (**b**) fibres grinded as powder, (**c**) fibre powder and polymer pellet are placed side by side, just before the dry-blending process

until they became broken in tensile tests. Five specimens of each type of bio-composite samples were tested.

SEM Characterisation

Scanning Electron Microscopy (SEM) images of PCL/date palm fibre bio-composites' broken surfaces with a 5 mm × 5 mm dimension were taken using a Zeiss Evo ma10 equipment at different magnification scales. A thin layer gold coating was applied for 40 s with a Quorum Q150R Plus sputter coater on specimens before taking SEM images. The images were investigated to understand the distribution of fibres within PCL polymer matrix.

Water Contact Angle Measurements

A KSV CAM-101 machine equipped with a CAM 2008 software was used to measure the water contact angle of bio-composites' surfaces for revealing information about their surface wettability. Water droplets were placed at different positions of the same sample and 10 measurements were taken for calculating an average water contact angle value of each sample.

Differential Scanning Calorimetry (DSC)

DSC analysis of manufacture PCL/date palm fibre bio-composites were carried out in a TA Q 100 DSC equipment, using a heat-cool-heat method, wherein, the first heating cycle was started from − 60 °C to 80 °C, followed by a cooling cycle from 80 °C to -60 °C with a subsequent second heating cycle up-to 80 °C. For both heating and cooling cycles, the same heating or cooling rate of 10° C/min was used. The degree of crystallinity of samples was measured with the following equation, wherein, ΔH_f and ΔH_{f° are the heat of fusion per gm of bio-composite samples and 100% PCL crystalline samples respectively. ΔH_{f° was considered as 135.31 J/g for the degree of crystallinity calculation.

Degree of crystallinity,

$$Xc\,(\%) = \frac{\Delta H_f}{\Delta H_{f0}} \times 100\%$$

Thermogravimetric Analysis (TGA)

A TA Q 50 TGA equipment was used to investigate the Thermal stability and degradation behaviours of bio-composites in an air atmosphere in the temperature range from 30 °C to 700 °C at a heating rate of 20 °C/min.

Thermo-mechanical Analysis (DMA)

The thermo-mechanical properties of bio-composites were determined from 20° C to 45° C at a heating rate of 2° C/min, a 1 Hz oscillation frequency and a 20 µm strain amplitude, in a nitrogen gas atmosphere using a double cantilever mode DMA TA Q 800 equipment. From DMA experiments, both storage modulus (E_o) and loss factor (tanδ) were measured.

Results and Discussion

Tensile Properties Analysis of Dry-Blended PCL/Date Palm Fibre Bio-Composites

Figure 2a provides typical tensile stress-strain curve up-to breaking points of dry-blended PCL/date palm fibre bio-composites, while, Fig. 2b shows the tensile curves up-to 20% strain of all tested bio-composites, so that the initial tensile test response of PCL/date palm fibre composites can be seen clearly. Average tensile properties data are presented in Table 3. From them, it can be seen that 100% PCL plastic samples have high strain value which was found to decrease significantly with the addition of date palm fibres in its matrix. Only a 2.5% (w/w) date palm fibre addition into the PCL matrix made a huge decline in the strain (%) values compared to the 100% PCL samples. A further continuous decrease was also noticed with the increase of date palm fibre percentage in the main polymer matrix; between them,

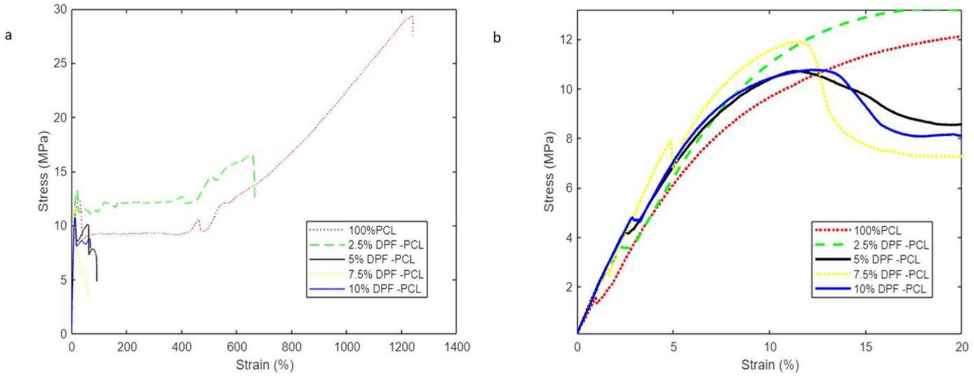


Fig. 2 (**a**) Tensile stress-strain curves of dry blended PCL/date palm fibre bio-composites (**b**) Tensile stress-strain curves up-to 20% strain for all bio-composites

Table 3 Tensile properties of dry blended PCL/date palm fibre bio-composites

Sample types	Tensile maximum strength (MPa)	Tensile strain at break (%)	Tensile modulus (MPa)
100% PCL	14.431 (±2.897)	1400 (±244.644)	148.975 (±0.487)
2.5% DPF-PCL	12.318 (±1.593)	346.674 (±336.644)	176.372 (±12.668)
5% DPF-PCL	9.164 (±1.819)	74.135 (±43.663)	183.25 (±20.179)
7.5% DPF-PCL	9.757 (±2.316)	46.836 (±15.026)	196.086 (±20.466)
10% DPF-PCL	9.649 (±0.917)	48.836 (±14.409)	198.005 (±19.630)

the higher fibre percentage – 7.5% and 10% fibres (w/w) showed very similar strain values of dry-blended PCL/date palm fibre bio-composites. Based on this observation, it can be said that perhaps a further increase of fibre contents into the polymer matrix might not reduce the strain values very sharply, which needs to be confirmed with experimental work in a future research.

The observed strain value decrease is not unexpected, since the fibre addition in the polymer matrix creates inhomogeneous structure and a poor adhesion at fibre-polymer interfaces which brings brittleness or reduction in the strain values. In opposite, tensile modulus was seen to increase with the increase of fibre addition percentages. In this work, the 100% PCL sample modulus was found within the expected range. The 2.5% DPF-PCL bio-composites showed a tensile modulus of 176 MPa which was almost a 20% increase compared to only PCL samples. The highest modulus (198 MPa) was found for the 10% DPF-PCL bio-composites and this was very close to the modulus value of the 7.5% DPF-PCL bio-composites. For maximum strength data, a decline of strength values up-to 33% was determined for the 10% DPF-PCL samples compared to their 100% PCL bio-composite counterparts. From these tensile data, it is obvious that the fibre increases the resistance to tensile force in the PCL matrix at the start of tensile loading, resulting in an increase in the dry-blended composites' modulus values, which was not continued for long to support an increase in the maximum strength values, because of the significant drop in the ductility properties of the PCL matrix as found in strain data of tested bio-composites.

SEM Images of Dry-Blended PCL/Date Palm Fibre Bio-Composites' Fractured Surfaces

SEM image analysis was employed to understand the fracture surface morphology under tensile loading and fibre distribution in the dry blended PCL/date palm fibre bio-composites. All composite types were investigated, although images from only 2.5% DPF-PCL and 7.5% DPF-PCL bio-composites are included in Fig. 3, since all bio-composite types showed a similar result. Fracture surface features support the findings of tensile tests of bio-composites in this work. From SEM, it is obvious that 2.5% DPF-PCL bio-composite has less fibre contents compared to 7.5% DPF-PCL samples, as expected. Fibre content has a direct impact on tensile properties [30], as observed in this work. Fibre powders were not found distributed throughout the PCL matrix, instead, a fibre rich and fibre less areas were identified due to the agglomeration of fibre powders and this effect was more obvious with 7.5% DPF-PCL specimens. The irregular distribution of fibre powders created a less adhesion at fibre powder-polymer interfaces [1, 31, 32]. Also, their hydrophilic (fibres) – hydrophobic (PCL polymer) polarities were responsible for their less adhesion.

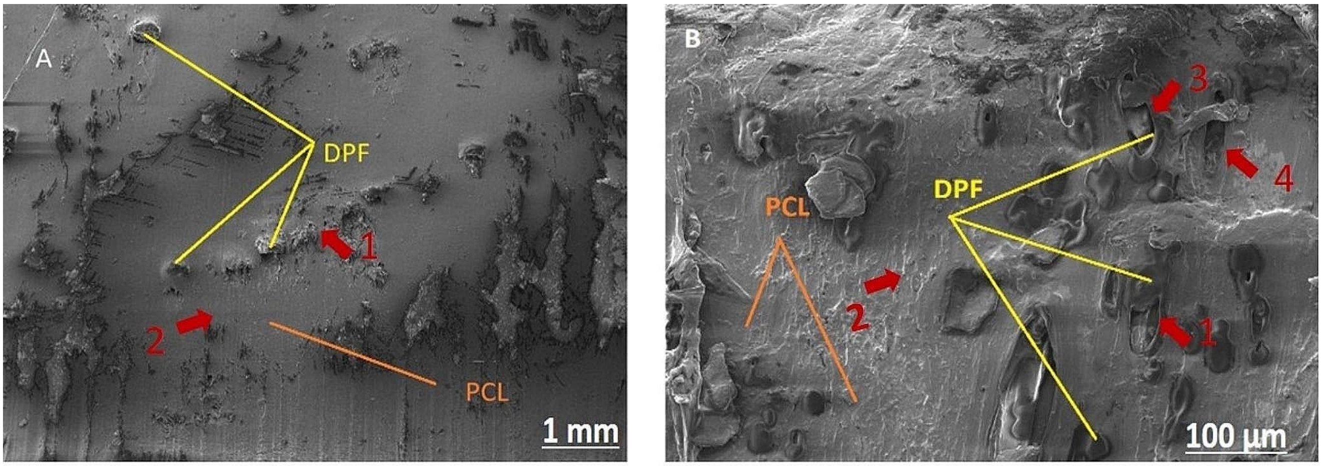


Fig. 3 SEM images of (**A**) 2.5% DPF-PCL and (**B**) 7.5% DPF-PCL bio-composites' fracture surfaces. DPF and PCL matrix are shown where they are abundantly seen in images. (1–4) number markings provide different information, 1 = DPF fibre rich area; 2 = PCL matrix rich area; 3 = debonding of fibre/matrix interface; 4 = fibre pull out

Brittle failure feature was seen in both Fig. 3 (a, b), since the fibres were found broken clearly and the PCL matrix surface showed very close to smooth failure surface. In Fig. 3b, the debonding between the fibre-polymer interface was noticed and also, fibre pull out was occurred under tensile loading scenario. Based on these fracture surface features, it is clear that fibres provided some support to the PCL matrix to increase the mechanical properties, such as tensile modulus with an increasing fibre content, but due to a poor fibre-matrix adhesion interface the brittleness was increased of produced bio-composites. This observation supports the determined tensile properties in the earlier section.

Water Contact Angle of PCL/Date Palm Fibre Bio-Composites

Water contact angle measurements provide information on hydrophilic or hydrophobic nature of polymer material surfaces linking to the relative wettability of materials [33, 34]. In our work, this was measured through placing water droplets on bio-composite surfaces and capturing the angle between water droplets and bio-composite surfaces.

From Fig. 4, it can be seen that only PCL moulded samples have 77° water contact angle which is found very similar, but slightly lower, to the values reported in literature [35] This could be due to the manufacturing of PCL based substrate through different manufacturing processes, such as compression moulding vs. solvent casting. Differences in manufacturing processes may increase surface roughness and this might have decreased the water contact angle values of compression moulded 100% PCL samples in this work. The date palm fibre incorporation reduced contact angles proportionally with their relative contents in PCL matrix bi-composites. Date palm fibres are hydrophilic and it is expected that their addition in PCL matrix had increased the composite surface roughness and these reasons were responsible to reduce the water contact angle of date palm fibre/PCL bio-composites. For 2.5% and 5% date palm fibre-based composites, similar contact angles were measured to only date palm fibre contact angle, reported at 66°±3° [36] in other works in the literature. The lowest water contact angle was noticed for the 10% DPF-PCL composites wherein the highest fibre content was used.

Analysis of DSC Results

Figure 5 (a - b) shows heating and cooling cycles of DSC analysis for providing information on melting and non-isothermal crystallisation behaviours of PCL/date palm fibre bio-composites respectively. The melting temperature of only PCL and 2.5% DPF-PCL composites were found very close to each other, while, 10% DPF-PCL samples showed a slightly lower melting temperature. This could be related to the significant reduction in the crystallinity percentage of 10% DPF-PCL sample. The crystallinity was also found to reduce for the 2.5% DPF-PCL bio-composites compared

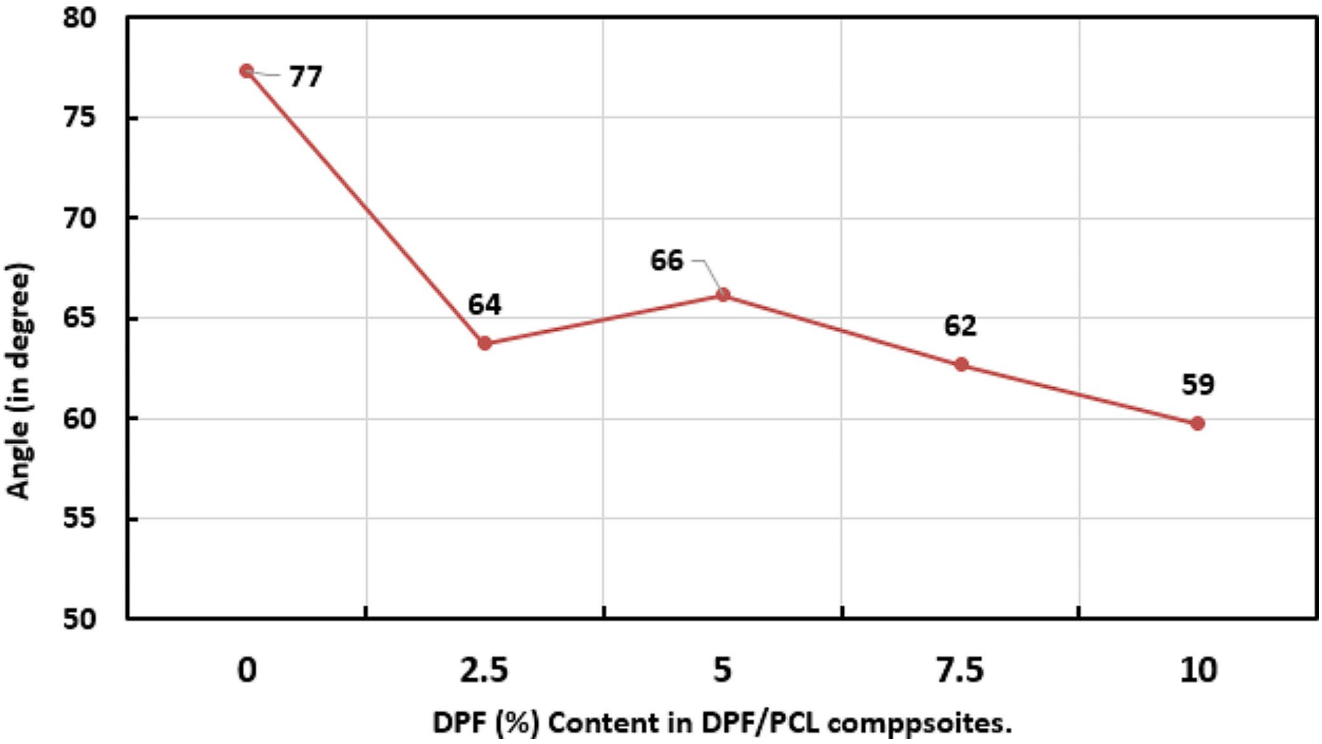


Fig. 4 Water contact angles of PCL/date palm fibre (DPF) bio-composites

Fig. 5 DSC analysis of bio-composites –heating cycle (**a**) and cooling cycle (crystallisation) (**b**)

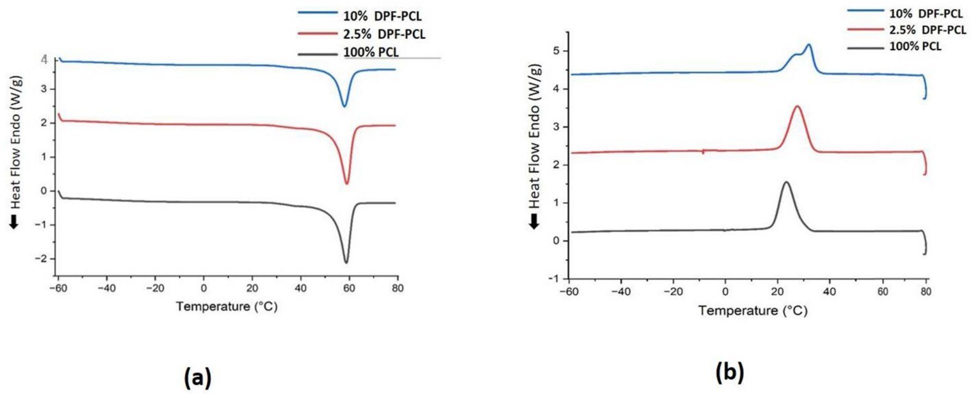


Table 4 DSC analysis data for melting and crystallisation behaviour of PCL/date palm fibre bio-composites

Samples	Melting		Crystallisation			
	Melting temperature (T_m, °C)	Crystallinity (%)	On-set temperature (T_0, °C)	Peak temperature (T_c, °C)	Crystallisation time (s)	
					Half time ($t_{1/2}$)	Full time
100% PCL	58.86	55.40	33.82	23.46	62.16	104.34
2.5% DPF-PCL	59.01	53.75	36.46	27.69	52.62	108.30
10% DPF-PCL	57.96	33.08	38.60	31.95	39.90	118.08

to 100% PCL samples, but not as significant as 10% DPF-PCL samples. Non-isothermal crystallisation analysis was carried out at only 10° C/min cooling rate to understand the crystallisation behaviour of developed bio-composites in this work. It is very obvious that the crystallisation on-set shifted towards higher temperatures with increasing fibre contents in PCL-DPF composites compared to only PCL samples. The crystallisation rate was also faster due to the incorporation of fibres into PCL matrix, which can be found from crystallisation half-time data (Table 4).

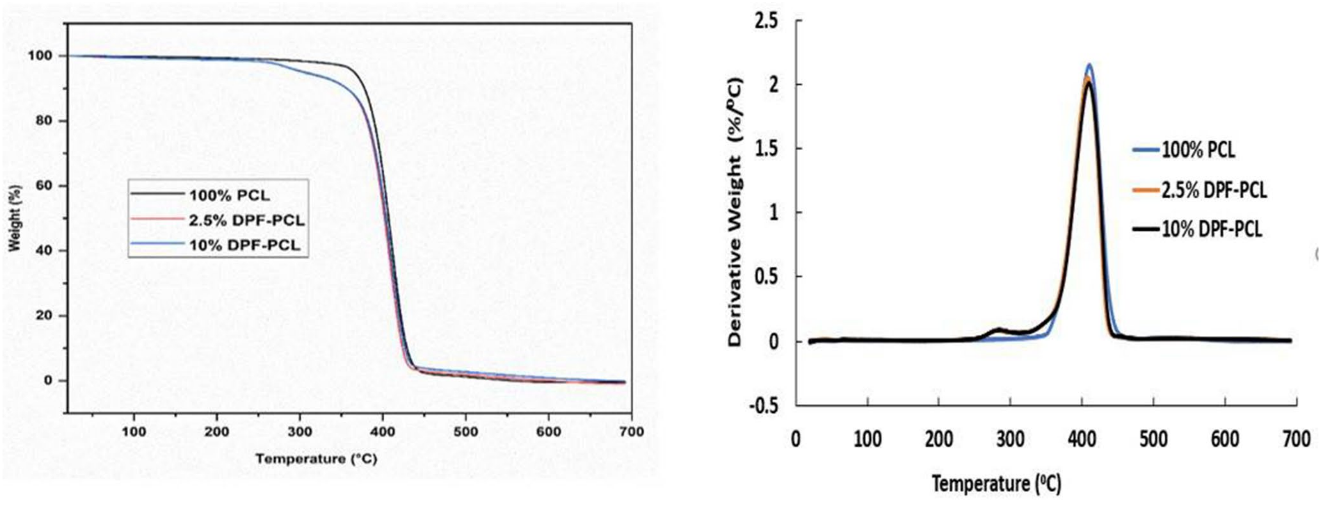
In this work, the crystallisation half-time was measured based on the time taken from the on-set of crystallisations to the peak of crystallisation of samples. The faster crystallisation half-time, higher crystallisation on-set and peak temperatures were also found for other natural fibres, such as flax [37] or sisal fibre [38] based polymer bio-composites in previous works reported in the literature. Date palm fibre surfaces acts as nucleating sites in PCL matrix that accelerates the crystalline growth, although date palm fibre incorporation didn't increase the overall crystallinity compared to 100% PCL samples. Because, the fibre surface also complicates the crystallization process at the same time with the promotion of a slow additional secondary crystallisation process [39], which was quite obvious for 10% DPF-PCL bio-composites from their second shoulder in the crystallisation peak temperature. Moreover, the overall crystallisation time was found higher for date palm fibre composites because of this secondary crystallisation, which basically was occurred to improve the crystalline order of bio-composites.

TGA Results Analysis

TGA curves show that the degradation in DPF-PCL bio-composites starts earlier unlike only PCL samples. This was occurred due to the fibre incorporation in PCL matrix. The similar finding was also reported for flax fibre-based bio-composites [37] Date palm fibre generally shows thermal degradation in three stages [40, 41] - the first stage is between room temperature to 110 °C relating to the moisture loss within the fibre structure; the second stage happens at 280 °C linking to the low molecular weight hemicellulose degradation and finally, the third stage is for the cellulose degradation at 360 °C. In our work, 2.5% and 10% DPF-PCL bio-composites showed similar degradation behaviours at 280° C and 360 °C for hemicellulose and cellulose degradation respectively, while, the moisture evaporation at around 100 °C was not found very obvious. Degradations at 280° C and 360 °C are also very vivid in DTG curves, wherein, at 280° C almost 10% weight loss or degradation was identified and at 360° the main degradation was occurred. 100% PCL samples showed only one degradation step at near about 360° C- 400° C (Fig. 6).

Dynamic Mechanical Thermal (DMA) Analysis

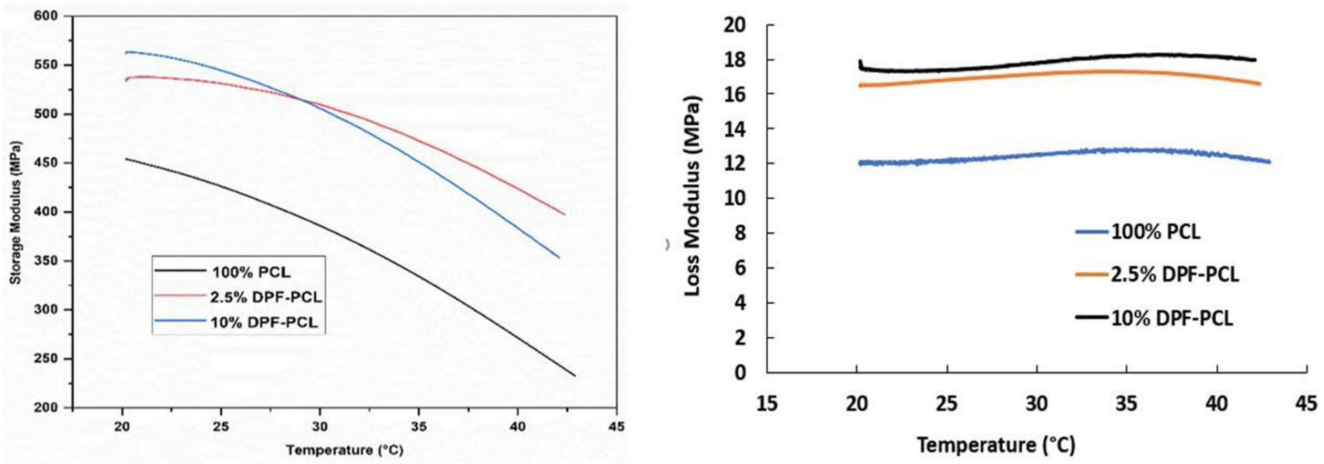
DMA graphs provide good information on stiffness and fibre-matrix interfacial adhesion of bio-composites [42, 43]. In Fig. 7 (a), date palm fibre addition in the PCL matrix increased the storage modulus according to their relative contents in both 2.5% and 10% DPF-PCL samples. This result also supports the tensile modulus increase of PCL/



(a)

(b)

Fig. 6 Thermogravimetric analysis of – (**a**) TGA and (**b**) DTG curves of DPF-PCL bio-composites



(a)

(b)

Fig. 7 DMA graphs of DPF-PCL bio-composites – (**a**) storage modulus and (**b**) loss modulus

date palm fibre bio-composite, described earlier. Although 10% DPF-PCL samples showed a higher storage modulus up-to 30 °C, they showed an opposite trend in the storage modulus value after 30° C compared to 2.5% DPF-PCL composites. In DSC results analysis, it was seen that the 10% date fibre contents promoted the secondary crystallisation in PCL matrix very obviously, which ultimately reduced the degree of crystallinity significantly compared to other date palm fibre-PCL bio-composites.

A higher fibre content in 10% DPF-PCL composites resisted more mechanical force initially and increased their elastic responses and hence, showed a higher storage modulus. But, with the increase of heating temperature, the molecular mobility of less crystalline PCL polymer in 10% DPF-PCL bio-composites also started to increase more, leading to a reduction in the storage modulus after 30 °C. Based on storage modulus curves, it was expected that only PCL samples would exhibit higher loss modulus values compared to fibre incorporated composites which was found totally opposite in DMA tests. 10% DPF-PCL composites had higher loss modulus compared to 2.5% DPF-PCL or 100% PCL samples. The observed higher loss modulus in bio-composites could be due to the fibre incorporation in polymer matrix which has better capability to dissipate energy in irregular fibre distribution and weak fibre-polymer interface in bio-composites.

Effects of Dry-Blending on Manufacturing of PCL/Date Palm Fibre Bio-Composites and a Literature-Based Comparison with Melt Blended PCL/Date Palm Fibre Bio-Composites

As discussed earlier, the dry-blending process removes an extra melt extrusion process from the compression moulding or other moulding based bio-composite manufacturing process. In our work, despite of having irregular fibre powders distribution in the polymer matrix due to the dry-blending process, the manufactured PCL/date palm fibre bio-composites demonstrated a very comparable tensile properties to melt-blended PCL/date palm fibre counterparts, reported in the literature. Dhakal et al. manufactured date palm fibre /PCL bio-composites and characterised their tensile and low velocity impact properties [21]. For a 20% date palm fibre in PCL matrix, they reported a tensile modulus of 284 MPa, strain of 21% and tensile strength of 24 MPa. In this work, tensile modulus, strain and tensile strength values were achieved as 198 MPa, 48% strain and 9.6 MPa respectively with a 10% fibre-based PCL bio-composites. Although, it is very difficult to compare directly these two different studies on PCL/DPF composites, it is expected that with the increase of date palm fibres up-to 20% in the current dry-blended composites, the modulus values will be increased and could be comparable to a value of 284 MPa. The reduced tensile strength in this work compared to the literature could be due to the differences in PCL polymer grade differences, since we used a very flexible PCL polymer grade for the bio-composite manufacturing. Therefore, based on this literature comparison, it can be said that the dry-blending process is capable of producing date palm fibre-PCL bio-composites with good mechanical properties through using less processing steps during blending and compression moulding processes. A further dry-blended compression moulding process optimisation could be investigated in future to improve a regular fibre distribution in polymer matrix by employing- (1) both polymer and fibres as powder materials at similar powder particle sizes for better mixing and (2) placing the dry-blended powdered fibre and polymer on compression moulding moulds using a distribution tool to evenly distribute the dry-blend throughout the whole moulds. In these ways fibre distribution regularities could be achieved, leading to an improvement in ultimate composites' mechanical performances. Dry-blending of date palm fibre in the polymer matrix showed similar thermal performances to melt blended natural fibres into different polymers (flax fibre in PCL, bamboo fibre in PCL and sisal fibre in PP), such as an insignificant reduction in thermal degradation resistance of bio-composites with reduced degree of crystallinity and the promotion of a slow secondary crystallisation in PCL polymer.

Design Implications for Sustainable Packaging Applications

It is hoped that the findings of this work will be helpful to promote the use of dry-blending process as an alternative to melt-blending process for manufacturing of PCL/date palm fibre bio-composites with good mechanical and thermal performances. The observed mechanical properties might be enough and could be used to carefully design PCL/date palm fibre bio-composites for sustainable packaging applications, wherein, mechanical load bearing demand is not a likely scenario and also the ductility property of packaging products is not the utmost priority. The thermal properties analysis also indicates that PCL/date palm fibre-based bio-composites can be easily used from a normal temperature to 40–45 °C. Considering both mechanical and thermal properties, some potential sustainable applications could be - disposable cutlery items, disposable plates, food container or tray mainly for cold, normal or slightly warm foods, packaging box for gift items or carrying vegetables/fruits/chocolates, small to medium size packaging trolleys or bags for storing or transferring components (electrical or DIY tools etc.) carrying very small amount of mechanical loads etc. For sustainable packaging products, barrier properties to moisture, oxygen and other gases with required functionalities are very important. In this regard, the observed less water contact angle of dry-blended PCL/date palm fibre composites is an indication of hydrophilicity with increasing surface roughnesses which might affect the deposition of barrier coating layer on surfaces positively [33] and hence, influence ultimate barrier properties of bio-composite packaging products. This warrants a detail investigation in future.

Conclusions

Dry-blended PCL/date palm fibre bio-composites were manufactured and their mechanical and thermal properties were investigated. Key findings are summarised as below-.

- Tensile modulus values showed an increase up-to 20% for the 10% DPF-PCL bio-composites, while, tensile strength and strain values were reduced compared to 100% PCL samples. The lower mechanical properties could be related to an irregular fibre distribution in dry-blended composite samples.
- The inclusion of date palm fibre affected the crystallisation in PCL polymer matrix, reduced the degree of crystallinity and promoted a secondary crystallisation process.

- TGA analysis showed a slight reduced thermal degradation performance for the fibre addition in polymer compared to only PCL samples. DMA results also supported tensile and thermal analysis findings.
- Dry-blended PCL/date palm fibre composites showed a comparable tensile and thermal properties with the melt blended PCL/date palm fibre bio-composites reported in the literature. A further dry-blending process optimisation should be carried out in future to improve a regular fibre distribution in polymer matrix leading to an improvement in their ultimate mechanical properties.
- Current findings and properties of dry-blended PCL/date palm fibre bio-composites could be carefully designed for various low mechanical load bearing or non-mechanical load carrying sustainable packaging applications.

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Declarations

Competing Interests Authors are declaring that there are no relevant financial or non-financial interests to disclose.

References

1. Yamini Jhanji, D.: *Natural Fibers: The Sustainable Alternatives for Textile and Non-Textile Applications*, in *Natural Fiber*, J. Han-Yong, Editor. IntechOpen: Rijeka. p. Ch. 1. (2022)
2. Gonzalez, V., Lou, X., Chi, T.: Evaluating environmental impact of natural and synthetic fibers: A Life Cycle Assessment Approach. Sustainability. **15**(9), 7670 (2023)
3. Al-Oqla, F.M., Salit, M.S.: *2 - Natural fiber composites*, in *Materials Selection for Natural Fiber Composites*, F.M. Al-Oqla and M.S. Salit, Editors. Woodhead Publishing. pp. 23–48. (2017)
4. Mohammed, L., et al.: A review on Natural Fiber Reinforced Polymer Composite and its applications. Int. J. Polym. Sci. **2015**, 243947 (2015)
5. Khan, S.H., et al.: *Characterization and Comparative Evaluation of Structural, Chemical, Thermal, Mechanical, and Morphological Properties of Plant Fibers*, in *Annual Plant: Sources of Fibres, Nanocellulose and Cellulosic Derivatives: Processing, Properties and Applications*, R. Khiari, M. Jawaid, and M.N. Belgacem, Editors. Springer Nature Singapore: Singapore. pp. 1–45. (2023)
6. Cheung, H., et al.: Natural fibre-reinforced composites for bioengineering and environmental engineering applications. Compos. Part. B: Eng. **40**(7), 655–663 (2009)
7. Shaikh, S., Yaqoob, M., Aggarwal, P.: An overview of biodegradable packaging in food industry. Curr. Res. Food Sci. **4**, 503–520 (2021)
8. Kumar, S., Darshna, A., Ranjan, D.: A review of literature on the integration of green energy and circular economy. Heliyon. **9**(11), e21091 (2023)
9. Das, A., et al.: A comprehensive review on recent advances in preparation, physicochemical characterization, and bioengineering applications of biopolymers. Polym. Bull. (Berl). **80**(7), 7247–7312 (2023)
10. Aaliya, B., Sunooj, K.V., Lackner, M.: Biopolymer composites: A review. Int. J. Biobased Plast. **3**(1), 40–84 (2021)
11. Fayomi, O.S.I., et al.: *Potential of bio-wastes in the development of composites for manufacturing application* Materials Today: Proceedings, 38: pp. 2353–2357. (2021)
12. Awad, S., et al.: A critical review on date Palm Tree (Phoenix dactylifera L.) Fibres and their uses in bio-composites. Waste Biomass Valoriz. **12**(6), 2853–2887 (2021)
13. Nasser, R.A., et al.: Chemical Analysis of different parts of date palm (Phoenix dactylifera L.) using Ultimate, Proximate and Thermo-Gravimetric techniques for Energy Production. Energies. **9**(5), 374 (2016)
14. Khandaker, S., et al.: From industrial jute fibre spinning wastes to biofibre-reinforced plastics. Mater. Chem. Phys. **313**, 128586 (2024)
15. AlMaadeed, M.A., et al.: Date palm wood flour/glass fibre reinforced hybrid composites of recycled polypropylene: Mechanical and thermal properties. Mater. Design. **42**, 289–294 (2012)
16. Augustia, V., et al.: Effect of date palm Fiber loadings on the Mechanical properties of High Density Polyethylene/Date Palm Fiber composites. Key Eng. Mater. **773**, 94–99 (2018)
17. Saifullah, A., et al.: Low velocity impact (LVI) and flexure-after-impact (FAI) behaviours of rotationally moulded sandwich structures. J. Mater. Res. Technol. **15**, 3915–3927 (2021)
18. Mousa, N., et al.: A New Green Composite based on plasticized polylactic acid mixed with date Palm Waste for single-use plastics applications. Polymers. **14**(3), 574 (2022)
19. Kharrat, F., et al.: *Extrusion blowing of composite films from poly(lactic acid) / date palm leaf filler for packaging applications: Preparation and Characterization*. (2021)

20. Umar, Y., et al.: Development and characterization of polyvinyl alcohol filled with date palm midrib powder. J. Thermoplast. Compos. Mater. **36**(4), 1437–1449 (2021)
21. Dhakal, H., et al.: Mechanical properties of leaf sheath date palm fibre waste biomass reinforced polycaprolactone (PCL) biocomposites. Ind. Crops Prod. **126**, 394–402 (2018)
22. Hejna, A., et al.: On the Correlation of Lignocellulosic Filler Composition with the Performance properties of Poly(ε-Caprolactone) based biocomposites. Waste Biomass Valoriz. **11**(4), 1467–1479 (2020)
23. Chiellini, E., et al.: Composite films based on Biorelated Agro-industrial Waste and Poly(vinyl alcohol). Preparation and Mechanical properties characterization. Biomacromolecules. **2**(3), 1029–1037 (2001)
24. Dev, B., et al.: Mapping the progress in natural fiber reinforced composites: Preparation, mechanical properties, and applications. Polym. Compos. **44**(7), 3748–3788 (2023)
25. Curling, S.F., et al.: Feasibility of using straw in a strong, thin, pulp moulded packaging material. Ind. Crops Prod. **97**, 395–400 (2017)
26. Sarasam, A.R., Krishnaswamy, R.K., Madihally, S.V.: Blending chitosan with polycaprolactone: Effects on physicochemical and antibacterial properties. Biomacromolecules. **7**(4), 1131–1138 (2006)
27. Urquijo, J., Guerrica-Echevarría, G., Eguiazábal, J.I.: Melt processed PLA/PCL blends: Effect of processing method on phase structure, morphology, and mechanical properties. J. Appl. Polym. Sci., **132**(41). (2015)
28. Abdellah, M.Y., et al.: Characteristic properties of date-palm fibre/sheep wool reinforced polyester composites. J. Bioresources Bioprod. **8**(4), 430–443 (2023)
29. Bourmaud, A., et al.: Exploring the potential of waste leaf sheath date palm fibres for composite reinforcement through a structural and mechanical analysis. Compos. Part A: Appl. Sci. Manufac. **103**, 292–303 (2017)
30. Saada, K., et al.: Exploring tensile properties of bio composites reinforced date palm fibers using experimental and modelling approaches. Mater. Chem. Phys. **314**, 128810 (2024)
31. Asim, M., et al.: Effect of surface modified date palm fibre loading on mechanical, thermal properties of date palm reinforced phenolic composites. Compos. Struct. **267**, 113913 (2021)
32. Ghori, S.W., Rao, G.S., Rajhi, A.A.: Investigation of Physical, Mechanical Properties of Treated Date Palm Fibre and Kenaf Fibre Reinforced Epoxy Hybrid composites. J. Nat. Fibers. **20**(1), 2145406 (2023)
33. Yorseng, K., et al.: Influence of Accelerated Weathering on the mechanical, fracture morphology, Thermal Stability, Contact Angle, and water absorption properties of Natural Fiber Fabric-based Epoxy Hybrid composites. Polymers. **12**(10), 2254 (2020)
34. Stark, N.M., Matuana, L.M.: Characterization of weathered wood–plastic composite surfaces using FTIR spectroscopy, contact angle, and XPS. Polym. Degrad. Stab. **92**(10), 1883–1890 (2007)
35. Li, T.-T., et al.: Preparation and property evaluations of PCL/PLA composite films. J. Polym. Res. **28**(5), 156 (2021)
36. Perera, H.J., Goyal, A., Alhassan, S.M.: Surface properties of alkylsilane treated date palm fiber. Sci. Rep. **12**(1), 9760 (2022)
37. Arbelaiz, A., et al.: Thermal and crystallization studies of short flax fibre reinforced polypropylene matrix composites: Effect of treatments. Thermochim. Acta. **440**(2), 111–121 (2006)
38. Joseph, P.V., et al.: The thermal and crystallisation studies of short sisal fibre reinforced polypropylene composites. Compos. Part A: Appl. Sci. Manufac. **34**(3), 253–266 (2003)
39. Huang, Y., et al.: Nonisothermal Crystallization Kinetics of Modified Bamboo Fiber/PCL composites. J. Appl. Polym. Sci. - J. APPL. POLYM. SCI., 116. (2010)
40. Bezazi, A., et al.: Investigation of the date palm fiber for green composites reinforcement: Quasi-static and fatigue characterization of the fiber. Ind. Crops Prod. **146**, 112135 (2020)
41. Al-Oqla, F., Hayajneh, M., Al-Shrida, M.: Mechanical performance, thermal stability and morphological analysis of date palm fiber reinforced polypropylene composites toward functional bio-products. Cellulose. **29**, 1–17 (2022)
42. Ahamed, B., et al.: High performance short jute fibre preforms for thermoset composite applications. Compos. Part. C: Open. Access. **9**, 100318 (2022)
43. Hasan, M., et al.: Improved mechanical performances of unidirectional jute fibre composites developed with new fibre architectures. RSC Adv. **11**(37), 23010–23022 (2021)