Design of flax fibre-reinforced PLA composites using microparticles: a strategy to improve interfacial bonding and dispersion

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Abstract:

Interest in using natural fibres, as alternatives to synthetic reinforcements in polymer matrices, is growing due to the ongoing rise in global warming and sustainability concerns. Because of their high strength-to-weight ratio, natural fibres are emerging as next-generation materials in the construction industry, such as insulated panelized building systems, plates and cellular beams. However, poor wettability and weak bonding at the fibre/matrix interface restrict the dispersion of natural fibres, resulting in the reduction of the composites' performance. Thereby, two collaborative strategies are employed in this research to improve fibre dispersion uniformity. In the first step, a thin film of TiO_2 is formed on the surface of flax fibres using a dip-spin coating approach, followed by confinement of the treated fibres between two PLA sheets. Under dip-spin coating, a larger surface area of TiO_2 was formed, resulting in improved interaction between TiO_2/PLA and TiO_2/fibre. The prepared TiO_2/flax fabric/PLA composites were mechanically shredded and sieved to generate microparticles with sizes between 315 and 630 µm. Composites of PLA/TiO_2/flax fibres were then prepared by loading 5% of microparticles into PLA. Differential scanning calorimetry (DSC) was used to evaluate the crystallization behaviour of the samples. The dispersion of fibres within PLA, as well as the effect of the applied treatment approach on the heterogeneous nucleation ability of the fibres, was investigated using polarized optical microscopy (POM). The observations indicated that grafting the fibres with a thin TiO_2 film, followed by pre-wetting with PLA, considerably improved fibre dispersion by preventing fibre–fibre agglomeration and enabling gradual incorporation into the matrix, while also promoting a higher degree of transcrystallinity at the fibre surface. The results of thermogravimetric analysis (TGA) showed that the TiO_2 thin film delayed the apparent thermal degradation of flax fibres compared to untreated fibres. Finally, dynamic mechanical analysis (DMA) results indicated that the storage modulus of the treated fibre composites improved due to enhanced interfacial adhesion between PLA/TiO_2 and TiO_2/flax fibres, facilitating more efficient stress transfer across the interface.

Keywords: *NFPCs, Dip-spin coating, Dispersion, Interfacial bonding, Crystallinity*

1. Introduction

Natural fibre-reinforced polymer composites (NFPCs) offer a sustainable strategy to reduce dependence on fossil resources and mitigate environmental pollution, while enabling the production of lightweight and cost-effective materials [1]. One of the most promising applications of NFPCs is in the construction sector, where natural fibres are particularly attractive for thermal insulation and acoustic performance, as well as in semi-structural and structural components such as floors, ceilings, and wall partitions [2]. They are also used as skins in insulated panelized building systems [3], and in various architectural elements, including doors, bridges, and fences [2]. Among natural fibres, flax is recognized as one of the most widely used and mechanically robust sustainable reinforcements for engineered polymer systems, owing to its relatively high tensile strength and favourable stiffness [4], [5]. Therefore, flax has been investigated as a potential material for load-bearing applications, such as plates and cellular beams, in polymer-based composites [7]. In recent years, increasing attention has been given to fully bio-based composite systems, particularly those combining natural fibres with biopolymers such as polylactic acid (PLA). These materials offer the potential to develop fully biodegradable and bio-sourced composites [1], [8]. Despite its environmental advantages, PLA exhibits several limitations, including a slow crystallization rate and relatively low melt strength [9]. These drawbacks can be effectively mitigated through reinforcement with natural fibres such as flax. Natural fibres can be used at different size scales in polymer-based composites, depending on the processing conditions. For instance, fibres shorter than 2 mm, typically below the size of pelletized compounds, are commonly processed using extrusion [10]. Additionally, it has been reported that short-fibre-reinforced composites exhibit improved PLA coating on pull-out fibres after fracture compared with long-fibre-reinforced systems, which is often attributed to their high aspect ratio [11]. Sieve analysis is a conventional technique for size classification. However, despite its simplicity, the sieving process poses challenges for natural fibres, particularly fibre entanglement within the sieve apertures [12]. More fundamentally, the primary challenge in using lignocellulosic materials, such as natural fibres, in polymer-based systems is their poor compatibility with polymer matrices. This incompatibility arises from the presence of strongly polar hydroxyl groups, which render the fibres inherently hydrophilic and thus incompatible with hydrophobic polymers [13]. Due to weak interfacial interactions, natural fibres tend to agglomerate, resulting in poor dispersion within the polymer matrix and consequently reducing the performance of the final composite. In addition, the relatively low thermal stability of natural fibres represents another limitation for their use in composite applications [14]. To address the outlined problems, chemical surface modification of natural fibres has been proposed as an effective strategy [15], [16]. In particular, coating TiO_2 as an amphiphilic interfacial layer on flax fibres has been shown to improve wettability and, consequently, enhance the interfacial strength between the reinforcement and the polymer matrix [17]. The physical characteristics of the coating layer, such as thickness, particle size (grain size), and uniformity, are critical parameters governing the formation and performance of thin films in composite applications. For instance, Aleksandra *et al.* [18] reported that coating TiO_2 onto lignin as a substrate resulted in a higher nucleation density and a shorter induction time compared with the direct addition of TiO_2 to the system. This behaviour was attributed to two main factors. First, lignin acted as a supporting substrate for TiO_2, reducing particle agglomeration and promoting a more homogeneous dispersion of TiO_2 particles, thereby increasing the number of available nucleation sites. Furthermore, the thickness of the coated film plays a significant role in determining the quality of interfacial adhesion between the fibre and the polymer, as well as the efficiency of load transfer [19]. Dip coating, spin coating and a combination of them (dip-spin

coating) have drawn attention among the several strategies documented for creating thin film coating layers with controlled physical characteristics. Wang *et al.* [20] compared these three methods to coat TiO_2 onto aluminum oxide. The results suggested that the dip-spin-coated sample exhibited a thin, uniform structure and smaller grains than other coating approaches.

In light of the aforementioned challenges, including difficulties in sieving natural fibres, fibre/matrix incompatibility, poor dispersion, and limitations in final composite performance, this study adopts two main strategies. First, a dip–spin coating methodology is employed to precisely deposit a TiO_2 thin film onto the surface of natural fibres, enabling control over key physical characteristics of the coating layer. Subsequently, the treated fibres are pre-wetted with PLA by confining them between PLA sheets. This confinement facilitates the conversion of fibres into more particle-like forms, thereby improving the efficiency of sieve analysis. In addition, it promotes better dispersion of natural fibres within the polymer matrix, as the fibres are already partially wetted with PLA prior to processing. Overall, by implementing these strategies, this research aims to provide insights into optimizing natural fibre–reinforced polymer composites for advanced and sustainable material applications.

2. Experimentation

2.1.Materials

Flax fabric and 4032D granule-grade PLA were purchased from EasyComposite and NatureWorks, respectively. Other chemical materials were supplied by Fisher Science.

2.2.Methodology

2.2.1. TiO_2 thin film formation on flax fibre surface

Prior to TiO_2 deposition, the flax fibre surfaces underwent pretreatment and oxidation steps according to Foruzanmehr et *al*.[17], [21]. These pretreatments aim to enhance TiO_2 adhesion to the fibre surface by promoting the formation of strong complexes with the $–COO^-Na^+$ functional groups of cellulose. A dip–spin coating process was then employed to deposit a thin layer of TiO_2 onto the surface of the flax fabrics. For this purpose, the TiO_2 Sol was prepared according to Foruzanmehr et *al*.[17], [21] and the flax fabric was subsequently immersed in the Sol for a dipping time of 2 minutes. The coating process was subsequently followed by applying a centrifugal force at a spinning speed of 3000 rpm and an adjusted time of 20 min to ensure that TiO_2 was well distributed on the fabric's surface. Then, the coated fabric was oven-dried at 70 °C for 1 hour and at 95 °C for 5 minutes to evaporate the solvent and form a thin film of TiO_2.

2.2.2. Shredding and sieving

Prior to shredding, a sandwich structure was prepared using the coated fabrics (30 wt% flax fibre) by placing each fabric layer between two thin PLA films. The composites were then shredded for 30 seconds using a Thomas-Wiley laboratory mill (Model 4). Subsequently, microparticles with sizes between 315 and 650 µm were selected using sieves for solvent-assisted composite preparation.

2.2.3. Composite processing

PLA was dissolved in dichloromethane (DCM) at a 10:1 ratio at 70 °C for 2 hours. Subsequently, 5 wt% of microparticles were added to the PLA solution and stirred overnight. The resulting mixture was then cast into a silicone mould and placed in a vacuum chamber for 48 hours to allow complete evaporation of DCM. The solidified material was chopped into small pieces and

further processed into thin films by compression moulding at 180 °C, following the next pressure cycle: 5 minutes at 0 Tons (T), 3 minutes at 300 T, 1 minute at 0 T, 1 minute at 500 T.

2.3.Characterization

2.3.1. Optical microscopy

The dispersion of fibres within the polymer matrix and the nucleating ability of the composites were examined using an optical microscope equipped with a polarizer. Thin composite films, approximately 50 µm thick, were prepared by compression moulding at 200 °C for 2 minutes. To eliminate the thermal history of the PLA matrix, the samples were heated from ambient temperature to 200 °C at a rate of 10 °C/min and held isothermally for 3 minutes. They were then quenched at a rate of 40 °C/min to 130 °C and maintained at this temperature for 15 minutes. Following isothermal treatment, the films were placed on glass microscope slides and observed in transmission mode.

2.3.2. Dynamic mechanical analysis (DMA)

The storage modulus of the composite specimen was estimated at a constant strain of 0.1% and a frequency of 1 Hz. The specimens were heated up from 25 to 140 °C at a constant rate of 5 °C.min^{-1} in a TA Instruments DMA Q800 testing machine equipped with a single-cantilever device. A minimum of five specimens were tested for each condition.

2.3.3. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to evaluate the thermal and crystallization behaviour of composites. Samples were analyzed using a Discovery DSC 25 instrument under a nitrogen atmosphere with a heating rate of 10 ˚C/min and an initial mass of 10–12 mg. A minimum of 5 samples were tested for statistical analysis for each condition.

2.3.4. Thermal gravimetric analysis (TGA)

Differential thermal gravimetric analysis (DTG) was performed using SETARM Co under a nitrogen environment with a heating rate of 10 °C/min and an initial mass of 12-15 mg.

3. Results and discussion

3.1. Thermal and crystallization characteristics

3.1.2. Differential Scanning Calorimetry (DSC)

Figure 1 presents the DSC thermograms of neat PLA and its composites, highlighting the glass transition temperature (T_g), cold crystallization temperature (T_c), and melting temperature of the samples. The degree of crystallinity (X_c) was calculated from the DSC data using the melting enthalpy (ΔH_m), cold crystallization enthalpy (ΔH_{cc}), and the heat of melting of the 100% crystalline PLA (91 J g^{-1}[22]) according to *Equation (1)*:

$$X_c(\%) = \frac{\Delta H_m - \Delta H_{cc}}{(1 - Wt\%_{fibre}) \times \Delta H_m^{\circ}} \quad (1)$$

The results indicate that the incorporation of microparticles containing untreated fibres led to a modest increase in crystallinity of approximately 3.2% compared to neat PLA (Table 2). This enhancement became more pronounced, reaching 8.9%, when the fibres were treated via the dip–spin coating method. Further evidence of enhanced crystallization is provided by the shift in cold crystallization temperature. As observed in the second heating cycle (Table 2), T_c decreased from 139 °C for neat PLA to 129 °C for the dip–spin coated sample (DIPSPIN-C). Since T_c reflects the ability of PLA chains to reorganize into crystalline structures during heating [23], this reduction

indicates accelerated crystallization kinetics. This behaviour can be attributed to the improved dispersion and surface characteristics achieved through the dip–spin coating process. In this method, TiO_2 particles are more uniformly distributed on the fibre surface and exhibit reduced particle size due to the applied centrifugal force, thereby increasing the number of effective heterogeneous nucleation sites. Consequently, cold crystallization is initiated at lower temperatures. Moreover, the reduced agglomeration of TiO_2 particles minimizes diffusion barriers for polymer chains, facilitating their rearrangement into ordered structures. The homogeneous dispersion of flax fibres throughout the matrix further contributes to the availability of nucleation sites, collectively lowering the energy barrier for crystallization and enhancing the overall crystallinity.

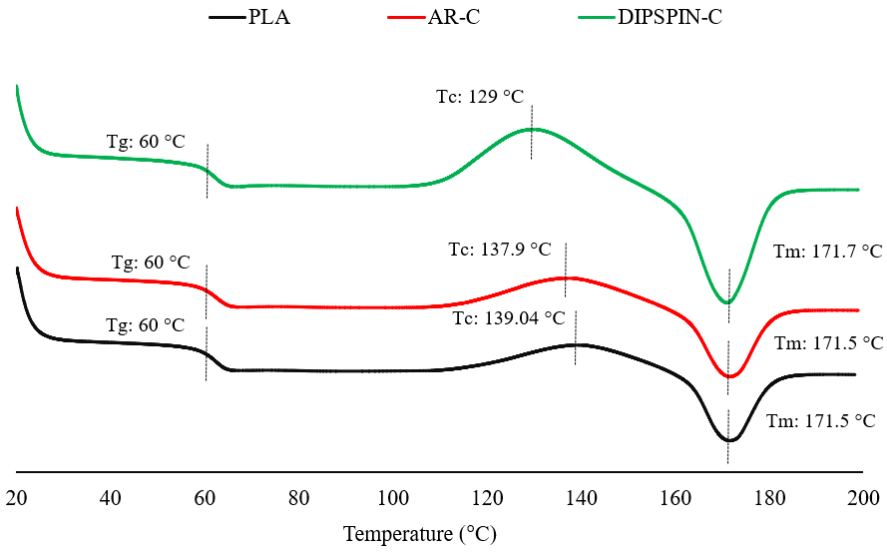

Figure 1. DSC thermograms of neat PLA and its composites.

3.1.2. Thermo-gravimetric analysis (TGA)

The overall thermal stability of neat PLA and its biocomposites with different interfacial characteristics was evaluated using thermogravimetric analysis (TGA). Figure 2 shows the weight loss profiles of the samples as a function of temperature. The temperatures corresponding to 10% and 70% weight loss were used as comparative indicators of thermal stability, and the results are summarized in Table 1. As observed, the incorporation of natural fibres reduced the thermal stability of PLA, which is consistent with previous studies [24]. This behaviour is primarily attributed to the lower thermal stability of natural fibres compared to PLA, such that partial replacement of the polymer matrix leads to an earlier onset of degradation. However, forming a TiO_2 coating layer improved the thermal resistance of the composites. For example, the temperature corresponding to 10% weight loss increased from 321.4 °C for the composite with untreated fibres (AR-C) to 325.1 °C for the dip–spin coated composite (DIPSPIN-C). This improvement can be attributed to the barrier effect of the TiO_2 coating, which may induce a temperature gradient within the material and delay the heat transfer, thereby shifting the degradation process to higher temperatures. The effectiveness of this coating is closely related to its microstructural characteristics. The dip–spin coating process promotes the formation of finer TiO_2 grains due to the applied centrifugal force, leading to an increased density of grain boundaries. According to the concept of interfacial thermal resistance (Kapitza resistance [25]),

these additional interfaces can hinder heat transfer by enhancing phonon scattering, thereby reducing thermal conductivity and slowing down thermal degradation. Furthermore, as discussed in Section 3.1.1, the TiO_2-coated fibres contributed to an increase of approximately 8.9% in the crystallinity of PLA, resulting in a more ordered and densely packed structure. This structural arrangement restricts polymer chain mobility and requires higher energy for thermal degradation, further contributing to the observed improvement in thermal stability. Finally, the relatively lower thermal stability of the composite containing untreated fibres can also be associated with fibre agglomeration, which may create localized regions of heat accumulation and initiate premature degradation. In contrast, improved fibre dispersion in the dip-spin coated system reduces such defects, contributing to the observed ~4 °C enhancement in thermal stability.

Table 1. TGA results for the temperatures corresponded to 10% and 70% weight loss.

	PLA		AR-C		DIPSPIN-C	
	10%	70%	10%	70%	10%	70%
Average of Temperature (°C)	339.82	366.41	321.41	347.04	325.12	350.84
SD	0.43	0.16	0.53	0.39	0.28	0.25
CV	0.00127	0.00044	0.00164	0.00115	0.00085	0.00071

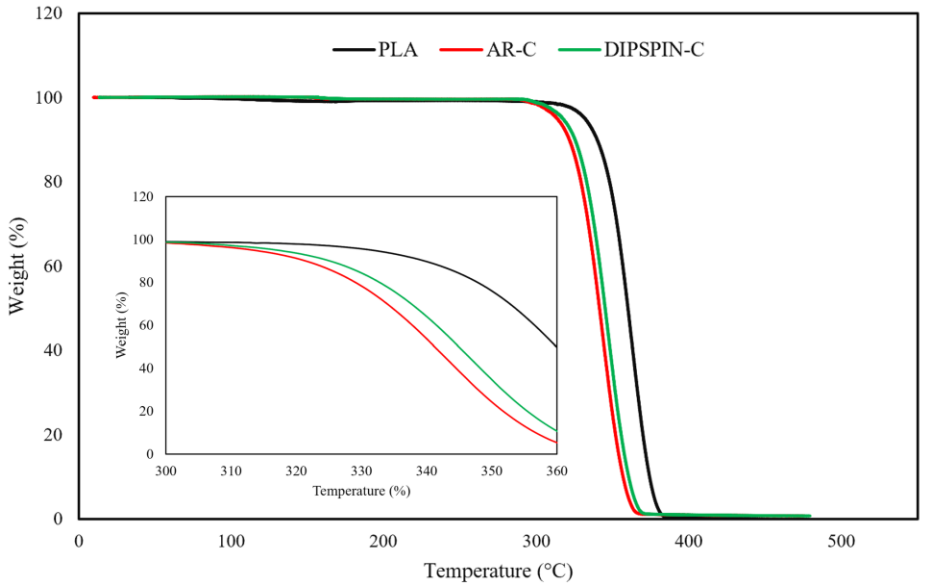

Figure 2. TGA thermograms of PLA and composites.

3.2. Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) is a powerful technique for evaluating the viscoelastic behaviour of composites and provides valuable insight into the fibre–matrix interfacial interactions [26]. Figure 3 shows the variation of storage modulus (E′) as a function of temperature for neat PLA and its composites. The maximum storage modulus values for all samples are summarized in Table 2. The storage modulus represents the elastic response of a material and reflects its ability to store and return energy [27]. As observed, in the glassy region (below T_g), the storage modulus of the dip–spin coated composite (DIPSPIN-C) significantly increased to 2823 MPa, compared to 1738 MPa for neat PLA. This value is also approximately 14.5% higher than

that of the composite containing untreated fibres. The enhanced stiffness can be attributed to improved interfacial adhesion between PLA/TiO_2, and TiO_2/flax fibres, which facilitates more efficient stress transfer across the interface [26], [28]. In addition, the increased crystallinity of PLA in the DIPSPIN-C sample contributes to the observed improvement in storage modulus. The crystalline regions act as physical crosslinks within the amorphous matrix, restricting chain mobility and resulting in a stiffer, more elastic material [29].

Table 2. Thermal and Dynamic-mechanical properties of PLA and composites.

		PLA	AR-C	DIPSPIN-C
DMA	Max. Storage Modulus (MPa)	1738.26	2466.4	2823.33
	SD	49.7	84.2	66.5
	CV	0.03	0.03	0.02
DSC	Degree of crystallinity (%)	22.5	25.7	31.4
	SD	0.11	1.17	0.72

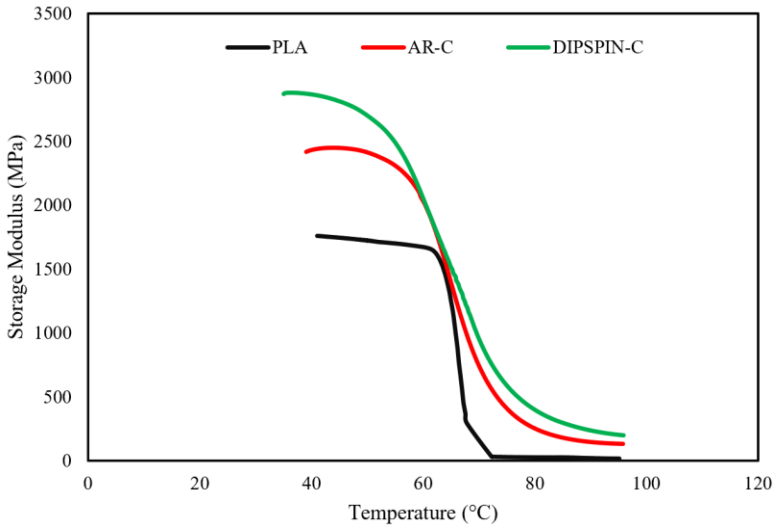

Figure 3. DMA storage modulus curves of PLA and composites.

3.3. Optical microscopy

The dispersion state of short fibres within the polymer matrix is a key parameter governing interfacial interactions and directly influencing the efficiency of stress transfer between PLA and natural fibres [29]. In addition, a well-dispersed fibre network provides a larger effective surface area for heterogeneous nucleation, thereby promoting the formation of crystalline regions within the polymer matrix. Consequently, as discussed in Section 3.2, improvements in dispersion are associated with enhanced mechanical properties. An optical microscope equipped with polarized light was employed to simultaneously evaluate the dispersion state of the fibres and the crystallization behaviour of the composites (Figure 4). The results indicate that treating the fibres with a thin TiO_2 interfacial layer, combined with partial encapsulation by PLA, significantly improves fibre dispersion within the matrix. As shown in Figure 4B, the DIPSPIN-C sample exhibits greater inter-fibre spacing, indicating reduced agglomeration, along with a higher level of transcrystallinity at the fibre surface compared to the AR-C sample.

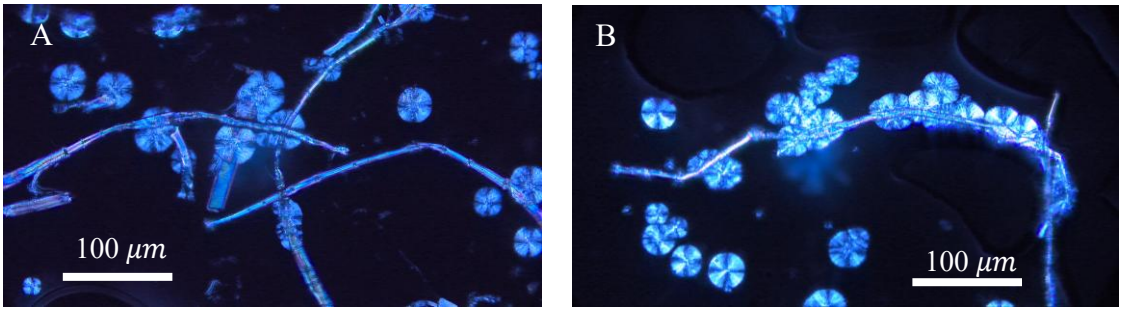

Figure 4. Optical microscopy results: (A) AR-C, and (B) DIPSPIN-C.

4. Conclusion

This study aimed to overcome the weak interfacial bonding and poor dispersion of natural fibres within the PLA matrix by adopting two key strategies: forming a TiO_2 coating layer on the fibre surface and subsequently encapsulating the coated fibres with PLA. The DSC results indicated that the total crystallinity of DIPSPIN-C increased by approximately 5.7% and 9% compared to AR-C and neat PLA, respectively. This enhancement suggests that a larger surface area for heterogeneous nucleation was generated as a result of the TiO_2 coating approach and the improved fibre dispersion. Although the incorporation of natural fibres reduced the overall thermal stability of PLA due to the inherently lower thermal stability of natural fibres compared to PLA, the enhanced crystalline structure restricted polymer chain mobility and required higher energy for thermal degradation, thereby contributing to the observed improvement in thermal stability. In addition, the shielding effect of the TiO_2 coating layer, together with the Kapitza effect associated with the fine-grained TiO_2 structure, likely contributed to the improved thermal behaviour. Finally, the enhanced storage modulus of DIPSPIN-C can be attributed to the improved interfacial adhesion between PLA/TiO_2 and TiO_2/flax fibres, which facilitated more efficient stress transfer across the interface. Moreover, the increased crystallinity of PLA acted as physical crosslinks within the amorphous matrix, restricting chain mobility and resulting in a stiffer and more elastic material.

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