Title: Thermo-rheological behavior of biopolymer and biopolymer blends for fiber spinning

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ABSTRACT

This study aims to develop an understanding of the thermo-rheological behavior of biopolymer and their blends for nonwoven applications. Specifically, evaluate the rheological behavior at low and high strains, study degradation kinetics, phase separation behavior, and thermal properties of various biopolymer and their blends, and finally correlate these fundamental parameters to fiber spinnability and mechanical properties of spun fibers. A comprehensive literature review of patents and peer-reviewed articles suggested that the rheological properties of biopolymers are confounded by hydrolytic and thermolytic degradation and this can influence the processing window available for fiber spinning and nonwoven production. Although considerable work has been done on characterizing biopolymers, there remains a significant knowledge gap in several areas such as (a) correlations between rheological parameters like relaxation time, Deborah number of each biopolymer, and their blends with fiber spinnability (b) Is there phase separation of blends under high strain rates encountered during fiber spinning (c) An understanding of the degradation kinetics and its impact on processing. This literature review report aims to fill in the knowledge gap present in the current research by conducting relevant investigations.

EXECUTIVE SUMMARY

Biopolymers serve as an environmentally sustainable substitute for conventional materials, derived from renewable biomass and exhibiting biodegradability in certain environments. Polylactic acid (PLA), polybutylene succinate (PBS), and polyhydroxyalkanoates (PHAs) are some examples of polymers currently utilized in food packaging and medical equipment. Implementing such blends for nonwoven applications is hindered by limited knowledge regarding the thermal, rheological, and phase separation behavior of the blends used for fiber spinning. Our study's objectives are 1) to evaluate the rheological behavior of biopolymer and their blends using steady-state shear and small amplitude oscillatory shear (SAOS) to determine the viscosity, and relaxation time as a function of temperature and blend ratio, 2) to obtain degradation profiles from thermogravimetric analysis (TGA) and examine the phase separation behavior using large amplitude oscillatory shear (LAOS) experiments, 3) characterize thermal properties such as glass transition temperature, crystallization rate and melting range of blends using differential scanning calorimetry (DSC).

A thorough literature analysis of peer-reviewed articles and patents related to the project provided several significant insights, detailed in this report. While considerable work has been done on characterizing biopolymers, the interest in biopolymers continues to grow exponentially. PLA is regarded as the most promising biopolymer due to its ease of processing, good characteristics, and comparatively cheaper cost compared to other biopolymers in the market. For PLA, the process of melt blending it with other biodegradable polymers is an easy and inexpensive way to give the biobased materials their suitable properties. However, a lack of understanding of the thermal, rheological, and phase separation behavior of the blends used for fiber spinning makes it difficult to implement such blends for nonwoven applications. The study of thermal and rheological properties of these blends is important as it affects fiber processability. Furthermore, phase separation in biopolymer blends may result in the finished nonwoven having poor mechanical properties. Therefore, this report aims to develop a thorough understanding of the application of these blends for nonwovens and conduct a detailed thermo-rheological investigation of biopolymer blends for melt spinning. Also, the examination of patents has provided insights into developing compatible biopolymer blends, most of which use rheological techniques to identify key processing variables.

This project is progressing according to the schedule outlined in the project proposal. Activities during the next period will focus on determining blend ratios of interest and developing biopolymer blends initially with PLA as the primary polymer, using dry blending or a single-screw compounder at NWI, characterizing rheological properties of blends using rotational rheometers and small amplitude oscillatory shear experiments and investigating hydrolytic and thermal degradation effects on rheological properties of PLA blends using SOAS experiments.

INTRODUCTION

Biopolymers serve as an environmentally sustainable substitute for conventional materials, derived from renewable biomass and exhibiting biodegradability in certain environments. In recent years, due to excessive dependence on conventional, petrochemical-derived polymers and their environmental effects has led to increased interest in identifying sustainable materials to reduce the present 66% [1] predominance of petroleum-based nonwoven products. Polylactic acid (PLA), polybutylene succinate (PBS), and polyhydroxyalkanoates (PHAs) are examples of such materials that are already used for food packaging, medical devices, and agricultural mulch [2].

The most researched biopolymer is PLA, which is known for its high tensile strength, modulus, and ease of processing and the lifecycle of PLA is depicted in Figure 1. However, PLA cannot be used in products that need high thermal stability since it is brittle and loses structural stability at high temperatures. Therefore, melt blending with other biodegradable materials is a simple and cost-effective method to give the biobased materials their desired properties [3]. The lack of understanding of the thermal, rheological properties, and phase separation behavior of the blends used for fiber spinning makes it difficult to implement such blends for nonwoven applications as these properties directly affect the processability of fibers. Furthermore, phase separation of biopolymer blends can lead to inferior mechanical properties of the final nonwoven.

Therefore, to develop a thorough understanding of the application of these blends for nonwovens, a complete thermo-rheological investigation of biopolymer blends must be conducted, building on the initial foundations laid in biopolymer blend structure-process-property relationships for melt spinning [3]. Methods for biopolymer blend production and fiber spinning, the study of viscoelastic properties of biopolymer melts using rheology, thermal and experimental characterization methods, and patent literature will be discussed in the report corresponding to the current research project, 23-271SB

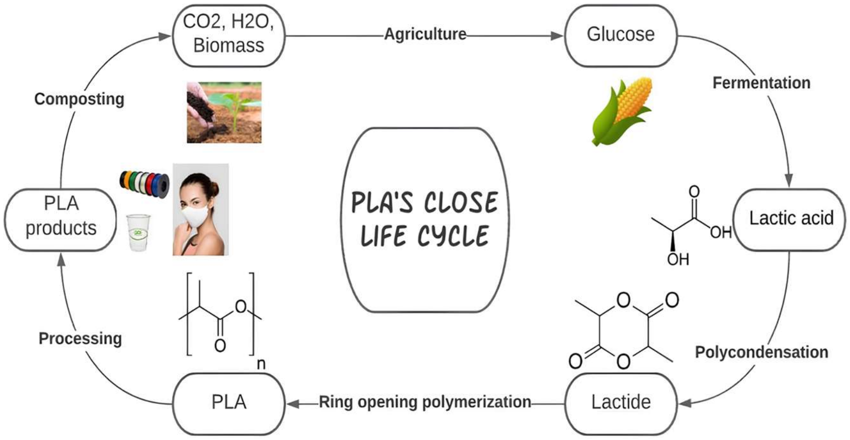


Figure 1. Closed Loop Lifecycle of Polylactic Acid [3]

OBJECTIVES

The literature is packed with PLA blends with other biobased polymers in sheets and films, but less research has been done on PLA-PBS and PLA-PHA blends in terms of thermal characterization and rheological properties of the blends for fiber spinning. Hence, this project aims to bridge the knowledge gap in biopolymer blend structure-process-property relationships and their thermo-rheological behavior.
The specific objectives for this project include:

- Investigate the effect of biopolymer blend degradation kinetics on the rheological properties
- Examine the phase separation behavior as a function of blend ratio and temperature
- Characterize thermal properties such as glass transition temperature, crystallization rate, and melting range of blends

This report aims to compile the conclusions from the literature, offering valuable information to guide this project's direction, predict its expected results, and understand the state-of-the-art at present.

LITERATURE REVIEW

There has been a significant focus on developing polyesters made from biomass that are derived from renewable resources such as PLA, PBS, and PHAs, due to a growing global concern for the environment. This interest has been driven by the desire to reduce the negative impact of traditional petroleum-based polymers and to promote the use of more sustainable alternatives [4]. Studies on these biopolymers have been mostly done in terms of characterizing them for film and packaging-based applications [5]. A comprehensive literature review has been carried out on biopolymer and its blends with PLA as the primary biopolymer and its fiber spinning for nonwoven applications. This review is composed of four sections; biopolymer blends and fiber spinning methods, rheological and phase separation behavior of polymer blends, experimental characterization methods, and patents.

Biopolymer Blends and Fiber Spinning Methods

There are two main methods for preparing PLA blends: 1) melt blending using single or twin-screw compounders, and 2) solution blending, which uses a solvent that dissolves every component, and the solvent will be evaporated after mixing. The physical structure, the required mechanical, thermal, or optical characteristics, and the miscibility of the blend components are important considerations that influence the choice of blending technique [6]. Melt blending is the process of blending two or more components at temperatures higher than each component's melting point [7]. The processing window spans from the end of the melting transition of the highest melting point to the decomposition temperature onset [8]. Melt blending is desirable because it is affordable and can be processed using commonly available technologies on an industrial and laboratory scale. The melt blending method does not include solvent contamination, in contrast to solution blending, and as a result, solvent removal is not necessary while preparing the blends.

Twin-screw extruders are preferred over single-screw extruders because they offer higher shear stresses, which are necessary for blending. Also, an important factor to consider while melt blending PLA with other biopolymers is that the pellets should be dried properly before mixing as PLA is subjected to degradation by hydrolysis [9]. SEM pictures of PLA blends containing 10 wt.% PHA and PBS are displayed in Figure 2. In studies conducted by Bhatia et al., it was found that PBS can be mixed with PLA up to a weight percentage of 20 while maintaining miscibility, but beyond 50 weight percent, phase separation occurs in the blend. Additionally, PLA tends to disperse in PBS at a 50/50 weight percent blend or higher [10]. The mechanical properties of the blends are reported in Table 1. The melt spinning setup and the schematic representation of the fiber spinning technique are shown in Figure 3.

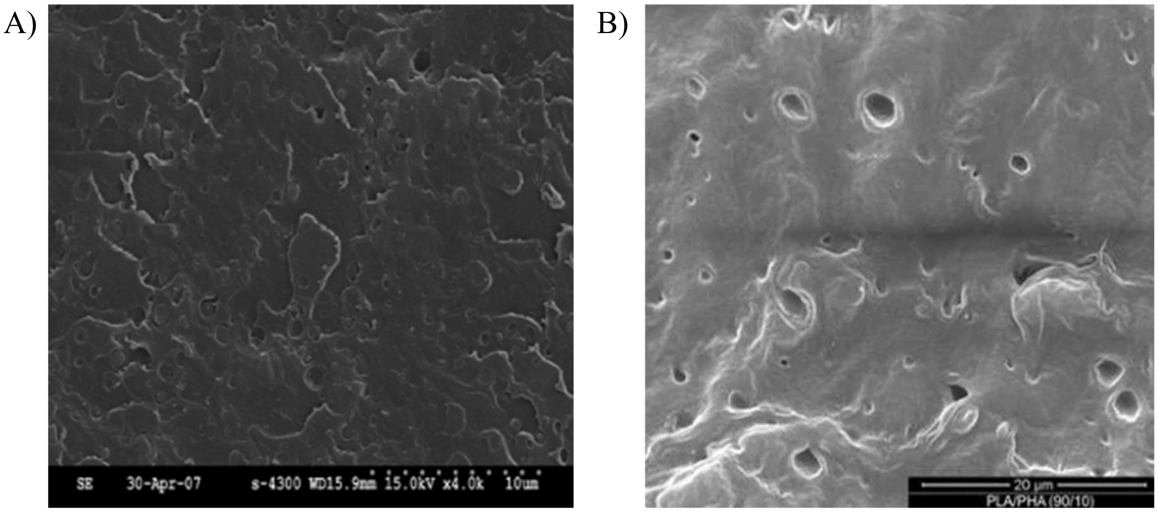


Figure 2. SEM micrographs of PLA/PBS (90/10) and PLA/PHA (90/10) blends, prepared via blending [10], [11]

Table 1. Mechanical properties of PLA, PHA, and PBS and their blends [10], [12]

Blend %	PLA/PBS 90/10			PLA/PHA 90/10		
	PLA (2002D)	PBS (G4460)	Blend	PLA (4032D)	PHA (PHI002)	Blend
Tensile strength (Mpa)	61	20	51	59	30	51
Tensile Modulus (Mpa)	1200	100	1050	3620	3810	3150
Elongation at break (%)	8	225	7	2.5	1.6	2.4

Finally, to relate fiber size and performance to throughput and spinning speed the literature has an important ratio known as Jill ratio. The Jill ratio links throughput to spinning speed and aids in the design of fibers that have specific diameters, process control, and the establishment of production constraints [13].

The Jill ratio is shown below in Equation 1.

Equation 1:

$$\text{Jill Ratio} = \frac{1000 \times \text{Throughput (ghm)}}{\text{Spinning Speed (m/min)}}$$

where ghm is the mass flow rate per capillary (g hole-1 min-1).

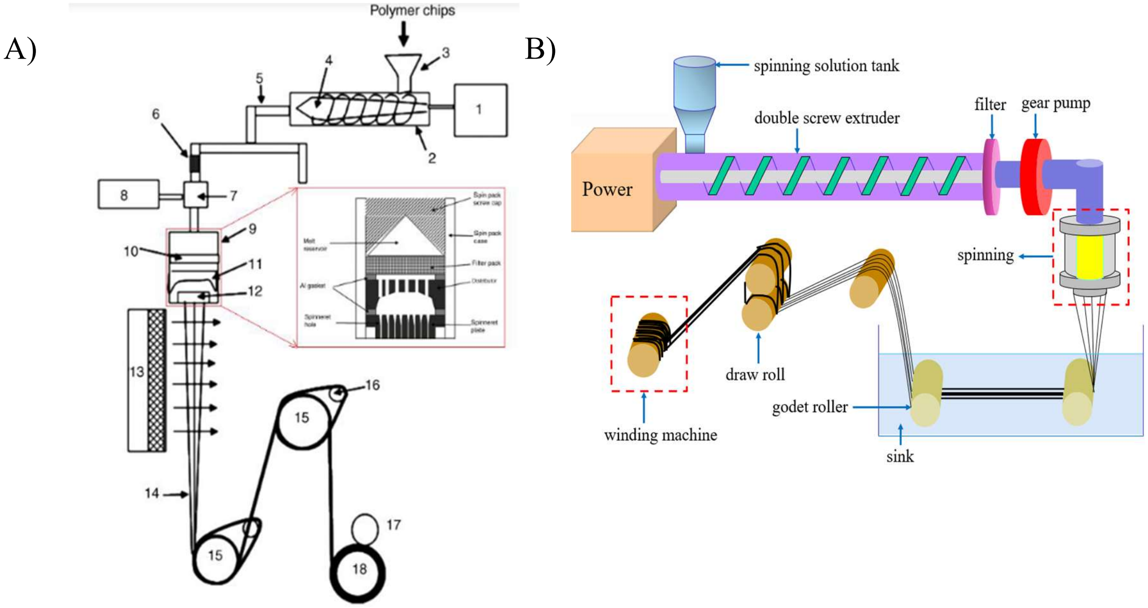


Figure 3. A) Schematic representation of melt spinning setup (1) extruder drive, (2)extruder, (3) hopper, (4) screw, (5) manifold, (6) static mixer, (7) metering pump, (8)metering pump drive, (9) spin pack, (10) mesh filters, (11) distributor, (12) spinneret, (13) cross-flow quench chamber, (14) freshly spun yarn, (15) godet, (16) idler roller, (17)friction-driven winder, (18) yarn bobbin [3]. B) Schematic drawing of fiber spinning apparatus [14]

Rheological and Phase Separation Behavior of Polymer Blends

Rheological measurements play a crucial role in understanding the flow and deformation behavior of polymer melts, which is essential for optimizing fiber spinning processes. Polymer melts, such as polylactic acid (PLA), display viscoelastic behavior, which combines the properties of viscous flow with flexibility. The viscosity of the polymer melt at extremely low shear rates is represented by the zero-shear viscosity, which is seen as a plateau at low frequencies. As a function of blend ratios and processing temperatures, steady shear studies have revealed information about the shear-thinning regime and zero shear viscosity (η_0). This experiment provides important information for determining processing shear rates as it can show if blending causes the shear thinning regime to begin earlier or be delayed in terms of shear rate [15]. Small Amplitude Oscillatory Shear (SAOS) experiments are a great tool for determining the relaxation time (λ) of blends by applying strains in the linear viscoelastic regime. The relaxation time represents the typical time scale that polymer chains take to relax when stress is applied and is determined by the intersection of the storage (G') and loss modulus (G") in a frequency sweep experiment. The ratio of λ with processing time (spent inside an extruder) gives us the Deborah number (De), a measure of viscoelasticity that is relevant for fiber spinning.

Figure 4 shows the varying degradation kinetics of different biopolymers, which can affect the processing window available for extruding these biopolymers into spun fibers as well as the rheology of the blends [16], [17]. The phase separation tendency of various polymer blends is an additional factor that must be taken into account for spun fiber mechanical performance and biopolymer processability. Therefore, understanding phase separation in biopolymer blends is critical from the rheological, thermal, crystallization, and mechanical standpoints [18], [19], [20]. Rheological studies previously showed steady shear viscosity profiles of different grades of PLA and their blends to describe the extrusion behavior. Researchers have found PLA blends with polystyrene (PS), and polypropylene (PP) exhibit shear-thinning behavior due to the alignment of polymer chain segments during melt flow, making them suitable for both extrusion and injection processes as their high viscosity at low shear rates ensures extrudate integrity while their low viscosity at high shear rates facilitates low injection temperature, pressure, and short injection cycle time [21], [22]. However, a thorough study examining the relaxation time of PLA and its blends has yet to be conducted to determine the optimal processing parameters for extruding spun fibers in nonwoven production.

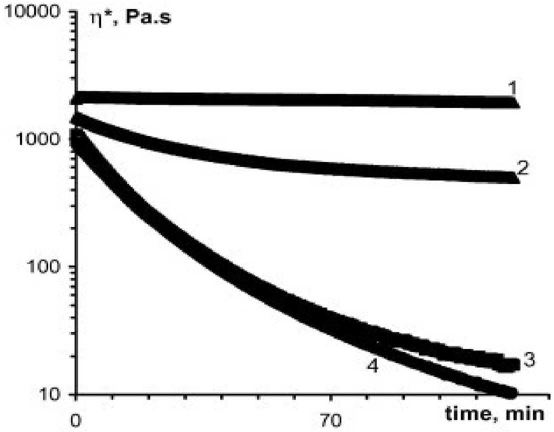


Figure 4. Complex viscosity as a function of time for PLA and a type of PHA, Poly-3hydroxybutyrate-co-3-hydroxy valerate (PHBV) under vacuum-dried and ambient storage conditions [16]

Phase separation is observed by SEM or optical pictures of the blends following SAOS tests, and it offers crucial details on the two polymers blend morphology and miscibility

[23]. The phase separation behavior of blends can, however, change under the high strains often encountered during nonwoven processing, which may have adverse impacts on the spun fibers processability and final properties [24]. However, the literature suggests that understanding phase separation under high strains is difficult using conventional techniques. Hence the emerging technique is the use of large-amplitude oscillatory shear (LAOS), in which a strain level is selected beyond the linear viscoelastic regime established using SAOS and by varying the frequency for the different PLA blends. A detailed protocol and analysis of LAOS data are described in detail in the literature [25]. As seen in Figure 5, the LAOS response for a miscible versus a phase-separated polymer blend due to the temperature difference is quite different and demonstrates a dual-peak stress response which may change according to degree of separation.

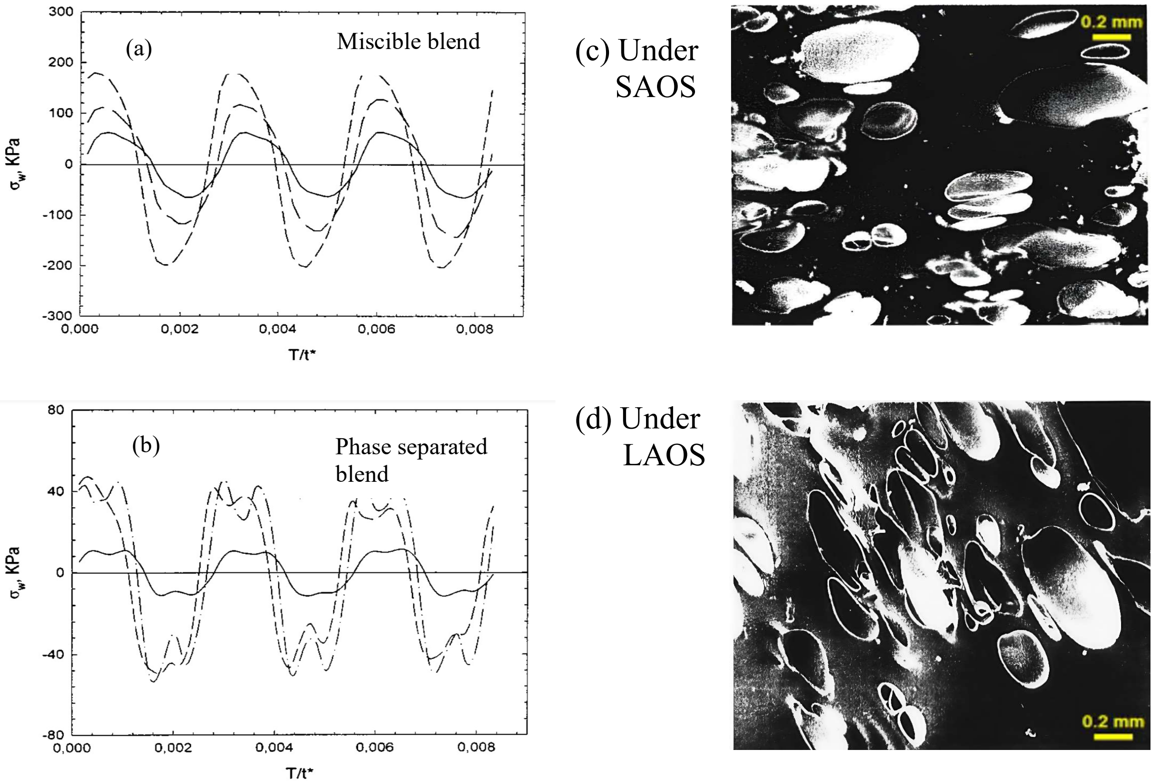
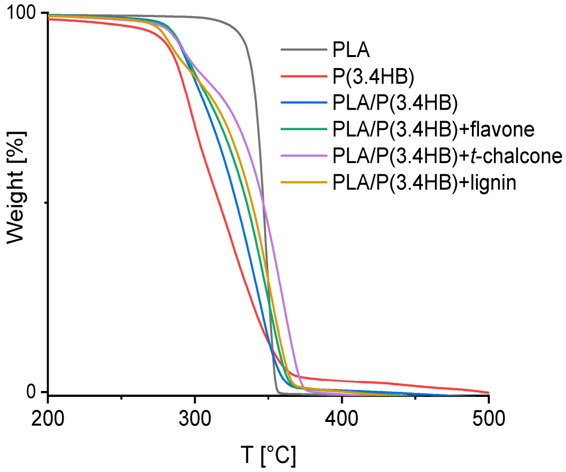


Figure 5. LAOS measurements for a 50/50 polystyrene-co-maleic anhydride/PMMA blend when (a) miscible and (b) partially phase separated. SEM images of the partial phase-separated blends under (c) SAOS and (d) LAOS conditions (fibrillar growth) [24]

PLA, PHAs, and PBS are biodegradable polymers that can break down when exposed to high temperatures and moisture through the processes of thermolysis and hydrolysis [26]. Their tendency to degrade at temperatures close to their melting point makes measure the fundamental melt properties. With the help of suitable rheological techniques, one can study the degradation kinetics of polymers at different temperatures. Gerard et al. assessed the thermal stability of PLA and PBS by observing the evolution of dynamic viscosity with time at fixed angular velocity [16].

Experimental Characterization Methods

Once rheological properties are well understood, the literature focused on thermogravimetric analyzer (TGA) and differential scanning calorimeter (DSC) analyses to understand the thermal behavior of biopolymer blends. TGA analysis was used to support the above-mentioned rheological degradation research as well as validate the degradation profiles of individual biopolymers and their blends. Figure 6 shows TGA graphs of aliphatic polyester blends with natural antioxidants [27]. The effects of blend ratios on the melting range and degree of crystallinity were verified using DSC. The bonding of nonwovens and the duration of bonding are greatly affected by crystallization, which is determined by the type of polymer and its melting range. Also, it has been noted that the use of polymers with slower crystallization kinetics and a larger melting endotherm improves the quality of thermal bonding and the bonding window of nonwovens made of polyolefins [28]. A measure, referred to as the crystallization rate coefficient (CRC) can be used for comparing the crystallization kinetics of different polymers. CRC is calculated by determining the cooling rate in °C/h needed to reduce the crystallization temperature by 1°C [29]. DSC graphs from Figure 7 represent traces of the Poly(L-lactide)/poly (butylene adipate) (PLLA/PBA) blends with a heating rate of 20 °C min^{-1} after quenching from the melt at a rate of 80 °C min^{-1} [30].



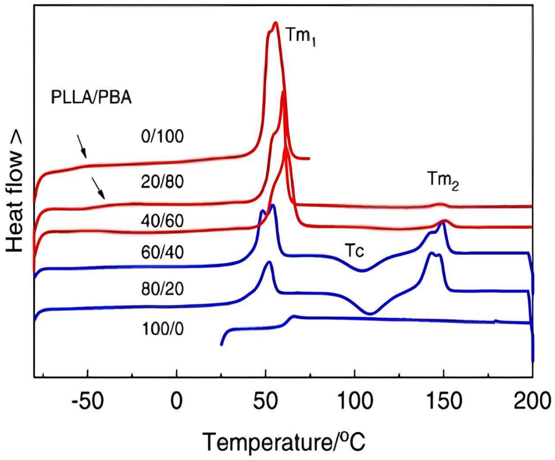


Fig 6. TGA curves of PLA [27]

Fig 7. DSC traces of PLLA/PBA blends [30]

Hence, the set of blends having the higher breath of melting distribution helped in broadening the bonding window. Therefore, a combination of a slower crystallization rate and a broader melting range is ideal to improve the bonding window. Thus, DSC can help identify potential blend ratios that may result in strong spun fiber structures. Andreassen et al. also noted that the tensile properties of nonwoven fabrics appeared to be controlled by the bonding characteristics of the individual fibers rather than the tensile properties of the fibers themselves [31].

Patent Literature

Over the past decade, there has been a notable increase in the development of nonwoven products involving biobased polymers, suggesting a greater emphasis on sustainable materials [32], [33], [34]. Several search engines, such as Google Patents and the Founders Legal AI-powered patent search tool, were utilized to gather related patents. A thorough search strategy was utilized, with particular search phrases such as "biodegradable polymer blends", "fiber spinning", and "nonwoven applications". The recovered patents were divided into two groups namely: compatible biopolymer blends and methods to enhance physical properties and processability.

Compatible Biopolymer Blends

Patents from Wesley Hale and Chakravarty et al., show the growing interest in creating biodegradable polymer blends that are compatible and have better processability. US patent 7,368,503 B2 by Wesley Hale in 2008 focused on creating certain biodegradable polymer blend compositions that provide better processability through extrusion and molding [35]. This invention relates to a blend of biodegradable polymers
comprising:
(A) about 5% to about 95% by weight of at least one flexible biodegradable polymer (A) having a glass transition less than about 0°C,
(B) about 5% to about 95% by weight of at least one rigid biodegradable polymer (B) having a glass transition greater than about 10° C, and
(C) about 0.25 to about 10 wt. % of at least one compatibilizer (C), said percentages being based on the total weight of the polymer blend; where the polymer blend has a higher zero-shear melt viscosity than polymers (A) and (B) separately.

US patent 7,989,062 B2 by Chakravarty et. al in 2011 developed a technique for combining polymers with high and low melting temperatures to create a polymer blend with a wider bonding window [36]. The background of the invention is that PLA nonwoven webs typically have a high roughness and low bond flexibility due to high glass transition temperature and slow crystallization rate of polylactic acid. On the other hand, polymers like PBS and PCL have a narrow bonding window, which makes it challenging to form a nonwoven web at high speeds. Hence, they proposed making of biodegradable nonwoven web that consists of multicomponent filaments. There are two components in multicomponent files: a first component and a second component. An aliphatic polyester with a melting point ranging from roughly 160°C to roughly 250°C is present in the first component, and a second aliphatic polyester is present in the second component but the second aliphatic polyester's melting point is around 30 °C lower than the first aliphatic polyester's melting point. The second aliphatic polyester has an apparent viscosity in the range of 50 - 215 Pascal-seconds measured at a temperature of 160° C and a shear rate of 1000 sec, the number average molecular weight between 30,000 and 120,000 Daltons, and a glass transition temperature of less than 25° C. They also used the disclosed blend in the production of the diaper top sheet.

Methods to enhance physical properties and processability

Significant documentation of the development of biobased polymers with improved physical properties can be found in patent literature. US patent 9,328,239 B2 in 2016 by Krishnaswamy et al. presents a method to combine PLA with several polyhydroxyalkanoates (PHAs), which have better mechanical qualities and can be manufactured in a wide range of temperatures [37]. The PLA/PHA compositions of the invention exhibit higher toughness compared to PLA compositions as the inclusion of the multiphase copolymer blend of PHA increases PLA's toughness. Also, these polymers exhibit unexpected synergies in melt rheology, thermal stability, processing, and mechanical properties, such as film processing and film properties, when they are melt-blended in the presence of a branching agent, such as organic peroxide. When comparing PHA blends made with reactive melt-blending to those made without it, the toughness enhancement was even more pronounced. Figure 8 shows the enhanced mechanical properties of the PHA blend in the composition.

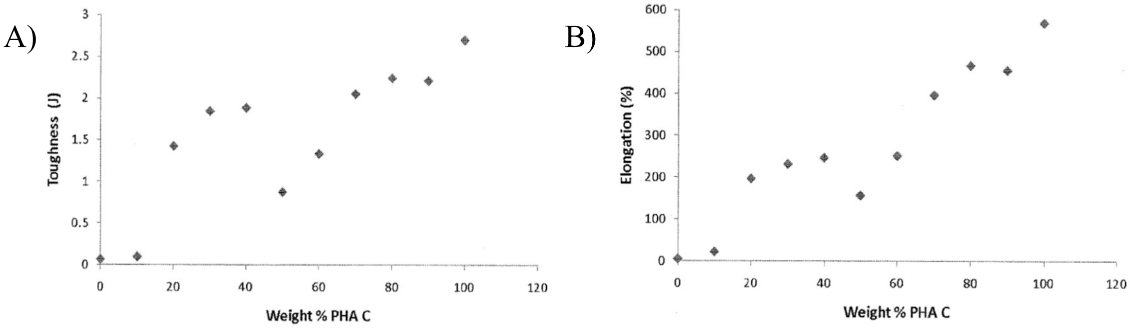


Figure 8. Increased mechanical properties of blend compositions A) elongation versus the weight percent of PHA blend B) toughness versus the weight percent of PHA blend [37]

The recent US patent 2022/0282030 A1 in 2022 by Choi et. al focuses on blending an antioxidant with lactic acid to produce a material with a high elongation percentage [38]. The patent presents a method for a biopolymer composition that can be mass-produced with high elongation and enhanced impact strength. One composition proposed in the patent includes a copolymer resin of lactic acid (LA) and 3-hydroxy propionate (3HP) in 83.5 % by weight or greater; an antioxidant; and a lubricant, wherein elongation of the biopolymer composition is great.

Conclusions from Patent Search

A great deal of work has been done to develop biopolymer blend compositions that allow for increased physical characteristics and processability based on the previous art search. But certain areas remain unexplored and there isn't any information available about the relaxation time, the degradation profile over time, large amplitude oscillatory shear studies, or the relevant processing window - all of which are important for determining how biopolymers might perform as nonwovens in the future.

SUMMARY & CONCLUSIONS

Biopolymers, particularly polylactic acid (PLA), polybutylene succinate (PBS), and polyhydroxyalkanoates (PHA), have gained significant attention in fiber-spinning applications due to their biodegradability and renewability. The thermo-rheological behavior of these materials and their blends is crucial for successful fiber production. PLA is the most widely used biopolymer for fiber spinning and exhibits good processability but suffers from brittleness and low heat resistance. Blending PLA with other biopolymers like PBS and PHA aims to overcome these limitations while maintaining biodegradability. From this literature survey, it is seen that PLA-PBS blends showed improved ductility and thermal stability compared to neat PLA. The addition of PBS lowers the viscosity of the blend, enhancing processability. However, the immiscibility between PLA and PBS can lead to phase separation, affecting the final fiber properties. While PLA-PHA blends demonstrated increased flexibility and impact resistance. The thermo-rheological behavior of these blends was highly dependent on the PHA type and content.

In summary, while considerable work has been done on characterizing biopolymers, there remains a significant knowledge gap in areas like what correlations exist between fundamental rheological parameters such as relaxation time, Deborah number of each biopolymer and their blends with fiber spinnability, an understanding of the degradation kinetics and its impact on processing, does phase separation of blends occurs under high strain rates during fiber spinning. The analysis of fiber spinning techniques and blend compositions from peer-reviewed articles and patent literature revealed new approaches to the creation and application of biopolymer blends for unique properties like enhanced elongation and tensile strength in nonwovens. The present study is highly relevant and significant to the industrial manufacturing of nonwovens utilizing blend compositions and thermo-rheological qualities, providing a multitude of advantages in properties.

FUTURE WORK

The initial subject and time planning for this project are as follows:

1.	Literature survey	Aug. 2024 – Dec. 2024
2.	Characterize rheological properties of blends	Jan. 2025 – June 2025
3.	Investigate hydrolytic and thermal degradation effects with SAOS experiments	Apr. 2025 – Sept. 2025
4.	LAOS experiments to determine high-strain phase separation behavior of select blends	Oct. 2025 – Mar. 2026
5.	Correlating thermal degradation profiles from TGA with rheology	Apr. 2026 – June. 2026
6.	Determine crystallization rate, develop spun fibers of the optimized blends, and evaluate mechanical performance	May 2026 – Dec. 2026
7.	Thesis & publications	Aug. 2026 – Nov. 2027

In compliance with the schedule, the literature survey has been completed. The next steps in the project will include determining blend ratios of interest and developing biopolymer blends, with PLA as the primary polymer, using a single-screw compounder at NWI. Once blend ratios are identified, rheological properties will be measured using the TA-Instruments DHR-3 Rheometer by small amplitude oscillatory shear (SAOS) experiments. Further phase separation tendency of biopolymer blends will be investigated using SEM and optical microscopy. Thermal degradation profiles will be obtained via TGA and the rate of crystallization will be identified with DSC to obtain blend ratios that may result in strong spun fiber. Finally, analyze the mechanical properties of spun fibers using a dynamic mechanical analyzer (DMA) attachment and compare the properties with conventional petroleum-based polypropylene (PP).

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