

MELT-SPINNING AND PROPERTIES OF SOY-FILLED
POLYETHYLENE, POLYPROPYLENE, AND POLY-(LACTIC ACID) FIBERS

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ABSTRACT

Sustainability concerns arising from the use of synthetic polymer-derived disposable nonwoven fabrics have prompted an interest in the development and use of disposable composite fibers by using renewable biomass as fillers. Agricultural materials are being investigated as fillers because these products are renewable and biodegradable. Prior literature studies have focused on the processing of bulk bio-filled polymers, mostly by compression and injection molding. Very limited studies have reported on soy-polymer fibers, and those fibers were spun by electro-spinning, i.e., the melt-spinning of soy-filled polymer fibers have not been systematically reported. Therefore, the melt-spinnability and properties of bio-composite fibers consisting of soy-filled polymers were investigated for the following three different thermoplastic matrices: (i) Polyethylene (PE), a widely used thermoplastic with a low melting point that minimizes thermal degradation of soy fillers; (ii) Polypropylene (PP), the most widely used thermoplastic in disposables, but one with a higher melting point than PE; and (iii) Poly-(lactic acid) (PLA), an expensive but a biodegradable thermoplastic with a slow degradation rate.

By adding soy flour (soy) to linear low-density polyethylene (LLDPE), soy-PE fibers with enhanced hydrophilic characteristics were developed. Blends containing only soy and LLDPE had limited draw-down, and the resulting thick fibers showed poor mechanical properties. When monoglyceride was added as a compatibilizer, thin fibers with good properties could be successfully spun due to improved dispersion of soy agglomerates in the LLDPE melt. Fibers spun from a blend containing 23/7/70 wt % of soy-monoglyceride-LLDPE displayed a tensile modulus and strength of 615 ± 38 and 57 ± 8

MPa, respectively. At 30% less synthetic content, these fibers still displayed mechanical properties generally comparable to those of base polyethylene fibers such as those used in nonwovens.

For nonwoven applications, physico-chemical properties are also relevant. Contact angle measurements showed that the soy-based fibers had a hydrophilic surface (contact angle of $33\pm 4^\circ$). Moisture absorption studies confirmed that soy-PE fibers gained about 20 wt % moisture in 1 h, whereas neat LLDPE fibers did not absorb any significant amount (LLDPE is hydrophobic). This hydrophilic behavior of soy-PE fibers mimics that of natural fibers. Presence of small soy agglomerates on the fiber surface also provides a textured surface and a desired tactile feel to the soy-PE fibers, which coupled with hydrophilic behavior indicates their potential use in disposable nonwovens.

Next, polypropylene (PP), was investigated as the matrix polymer because it is the most prevalent synthetic polymer used to produce fibers for nonwovens. Like PE, it is not biodegradable and has a processing temperature of 30°C higher than that of PE. The aim of this study was to investigate fiber spinnability and properties of soy flour-PP fibers as a function of processing temperature and filler content. An optimum processing temperature of 190°C was established, and fibers were successfully produced using a melt-spinning route that can be commercially scaled-up. Inclusion of soy-monoglyceride mixture at 15 wt% resulted in fibers with a tensile modulus of 914 ± 164 MPa and a tensile strength of 74 ± 7 MPa. Although lower than those of neat PP fibers (1224 ± 136 MPa and 104 ± 10 MPa), these SFM/PP fiber properties are large enough for nonwoven application. Further,

increasing soy content led to fibers with improved hydrophilicity and ease of coloring of the fibers.

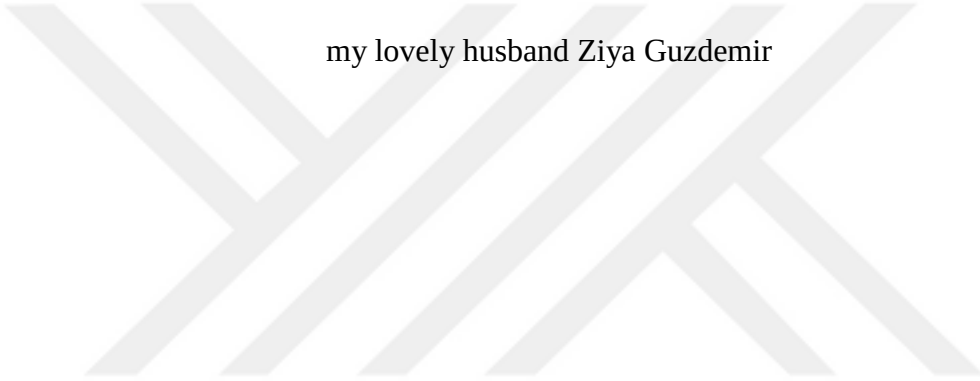
Poly (lactic acid) (PLA) has significant potential as a biodegradable replacement for petroleum-based plastics, but its high cost and slow biodegradability restrict its use in disposable products. The present study was aimed at reducing cost and increasing the degradation rate of PLA fibers by incorporating soy filler into it. After melt compounding of PLA with 5 wt% soy flour, continuous fibers were successfully spun via melt-spinning. Larger amounts of soy could not be incorporated due to the limited ductility that PLA possesses relative to its polyolefin counterparts. As expected for a particulate composite, the presence of particulate fillers led to a reduction of strength and strain-to-failure, from 74 ± 2 MPa and 48% for neat PLA fibers to 39 ± 5 MPa and 8%, respectively, for the soy-PLA fibers. The modulus remained unaffected at about 1 GPa for soy-PLA fibers. The soy-PLA fibers displayed a relatively rough exterior surface and provided a more natural-fiber feel. The overall degradation of soy-PLA fibers was accelerated about two-fold in a basic medium due to the preferential dissolution of soy that led to increased surface area within the PLA matrix. In summary, this research successfully established the melt-spinning of bio-composite fibers containing soy fillers in polyethylene and polypropylene (non-biodegradable base polymers) and poly-lactic acid (a biodegradable polymer). The properties of the fibers indicate the potential of melt-spun soy-filled fibers to be used as cost-effective bio-based fibers given that their properties are comparable to those obtained from neat polymers. It is recommended that future studies specifically investigate the formation and properties of non-wovens.

DEDICATION

To my precious daughter Nil Guzdemir

and

my lovely husband Ziya Guzdemir



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CHAPTER 1

INTRODUCTION

1.1 Overview of Polymer Use and Waste

In the last 60 years, world-wide plastics usage has increased from 1.5 million tons to 400 million tons¹ because plastics are low-cost materials that are suitable for a wide range of household application due to their ease of processing and durability. In the USA, the production of 51 million tons of plastics in 2018 was reported by the American Chemistry Council². Plastics improve the quality of life by contributing comfort, convenience, and safety. They are used in everyday products for long-term use such as housing, vehicles, toys, and furniture. Synthetic polymers also find significant short-term applications such as disposable medical devices, food packaging, utensils, diapers, and nonwoven hygiene products. The major advantage of plastics and the resulting disposables products is their affordability. Consequently, these inexpensive products have become ubiquitous. Unfortunately, the ease of disposability has also led to significant environmental pollution.

According to the Environmental Protection Agency, the average total municipal solid waste generated annually in the USA is around 258 million tons, of which 13% is plastic waste³. Of these, petroleum-based polyolefins are generated by major pollution problems. It is tough to give up the utilization and production of these polyolefin polymers

due to their excellent performance / cost ratio, but their massive annual production coupled with improper disposal has become a major societal problem.

The world has started to become more aware of sustainability issues and starting to follow the rule of “3Rs”, i.e., “reuse, reduce use, and recycle”. Plastic reusing and recycling are personal choices. Reusable plastics are mostly durable products, available in the market, which can be used over and over again. However, ‘reuse’ strategy (i.e., first “R”) is not applicable to sanitary items and food packaging due to the cleaning difficulties.

Plastics recycling can be done only when suitable facilities are available, and it is costly to build recycling centers. In the USA, only about 9% of plastic waste is recycled⁴, so recycling is not a complete solution by itself for alleviating plastic pollution problem. Also, recycled plastics lead to products that have inferior properties compared with virgin polymers. Moreover, recycling (the second “R”) is not feasible for disposable nonwoven fabrics/fibers such as those used for sanitary purposes. Thus, reducing synthetic polymer use, the third “R”, is an essential component of the overall solution. While eliminating the use of synthetic polymers is not an immediate solution, reducing the use of such polymers by substitution with biodegradable polymers or incorporation of bio-based fillers are potential solutions.

These environmental-friendly routes can be successful if the fibers so produced have similar properties and can be produced economically, as compared with those produced from their synthetic counterparts. Therefore, a brief summary follows that

discusses current fibers that are produced from synthetic polymers, their processing techniques, and their properties.

1.2 Polymeric Fibers for Disposable Nonwovens

The use of nonwoven fabrics has been increasing rapidly in a wide variety of applications, including medical, hygiene, automotive, packaging, apparel, filtration, furnishing, and safety products. The use of nonwoven fabrics in many textile areas provides essential features such as absorption, softness, strength, stretch, washability, sterility, and liquid repellency ^{5,6}. It is emphasized that only 30% of nonwovens are used as durable products ⁵, i.e., a large majority are used in disposable products. Also, in disposable nonwovens, synthetic fibers are preferred over natural fibers because synthetic polymers provide better elasticity, durability, light-weight, low-cost, and ready availability.

The production of synthetic polymers is dominated by polyolefins. Polypropylene (PP) is the most widely used polymer, with a global production of 127 million tons per year ⁷. In the nonwoven industry (a subdivision of the plastics industry), PP again dominates the market at 60%, as shown in Figure 1 (adapted from reference ⁸). Polyethylene (PE) is a close second, with a global production of 116 million tons per year ⁷.

As noted above, the vast majority of disposable nonwovens utilize synthetic fibers, with the bulk of these being polyolefins. So, PE and PP polymers are reviewed in this

section, followed by PLA, a biodegradable polymer with increasing commercial importance.

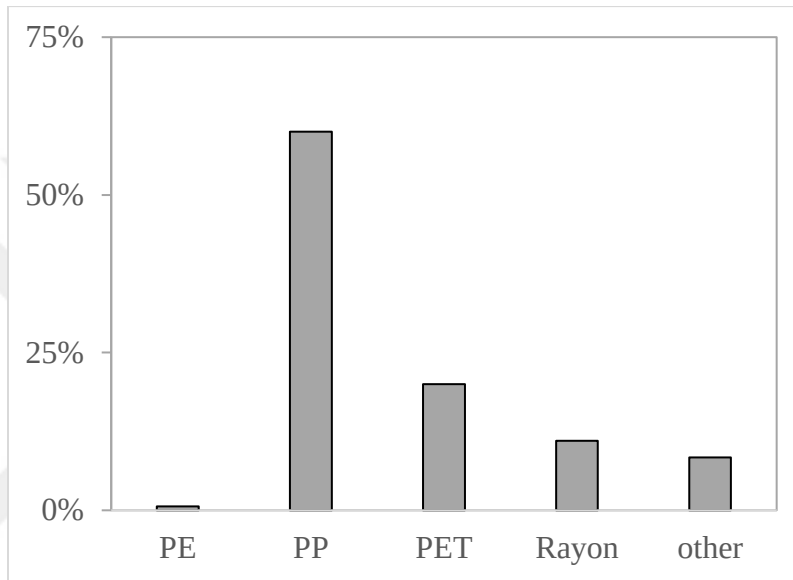


Figure 1. Market share of polymers used as fibers in nonwovens

1.2.1 Polyethylene

Polyethylene consists of long chains of ethylene ($-\text{CH}_2-\text{CH}_2-$) monomer and is a thermoplastic polymer that belongs to the polyolefin group. Polyethylene is classified into different types based on the branching type, the extent of branching, molecular weight, and density. The commonly used grades of PE in consumer products are high-density PE (HDPE), low-density PE (LDPE), and linear low-density PE (LLDPE). Structures of these polymers are schematically illustrated in Figure 2. HDPE consists of primarily long linear

chains that are not branched. Thus, tight molecular packing enhances its crystallinity and leads to a high (relative) density range of 0.94-0.97 kg/m³. LDPE consists of highly branched polyethylene with a density range of 0.91-0.93 kg/m³. LLDPE is a linear polymer with short branches, with a density range of 0.915-0.930 kg/m³. The melting temperature of PE ranges from 110°C for LDPE to 150°C for HDPE.

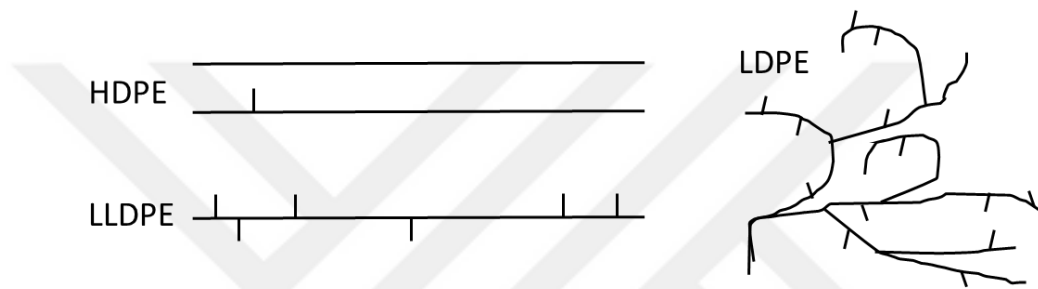


Figure 2. Schematic of the structure of the three main types of commercial polyethylene

PE is attractive because it offers excellent mechanical properties, chemical resistance, ease of processing, and low cost (\$0.90/kg). It is also very flexible and lightweight, with a ductility of around 500%. Some of the application areas are plastic bags, toys, and bottles. It is also used in the textile industry to produce marine ropes (because PE floats on water), fishing lines, sailing cloths, medical implants, and sports equipment.

1.2.2 Polypropylene

Polypropylene is the most produced/consumed synthetic polymer in the world. Polypropylene, long chains of propylene ($\text{CH}_3\text{-CH-CH}_2\text{-}$), is a thermoplastic polymer that also belongs to the polyolefin group. The melting temperature of PP is around 170°C. PP

has a semi-crystalline structure and so higher rigidity.^{9,10} PP has a density of 0.9-0.91 g/cm³.

PP is attractive because (like PE) it also offers excellent mechanical properties, chemical resistance, ease of processing, and low cost \$0.70/kg. The elastic modulus for polypropylene is between 1.0 – 2.1 GPa. PP solubility is low due to its apolar/ hydrophobic feature, so it is not easy to be wetted and dyed¹¹. It is commonly used in sports wear, diapers, food packaging, ropes, tapes, backpacks, and military wear.

1.2.3 Fiber Spinning

Fibers used to produce fabrics are mainly made by three different routes: wet-spinning, electro-spinning, and melt-spinning. In wet-spinning, a viscous polymer solution is injected through a spinneret into a coagulation bath that is used to extract the organic solvent and solidify the fibers^{12,13}. The wet-spinning route is not an environmentally friendly procedure due to the need for a large amount of organic solvents. Electro-spinning is a fiber-spinning technique that uses electrically driven jet of polymeric fluids¹⁴. To produce very thin fibers, most polymers require melting and fractional dissolution in nonpolar solvents. Also, electro-spinning is not the most environmentally friendly method due to the need for solvents^{13,15}.

Melt-spinning is an efficient and economical technique for producing polymeric fibers. Thermoplastics polymers, including polyolefins, are melt-extruded through a spinneret and then draw-down into fibers. It is eco-friendly, in that it does not require the

use of solvents, and is a low-cost method. A typical scheme of the melt-spinning process is shown in Figure 3 (adapted from reference ¹⁶). Polymer pellets are melted in an extruder and a down-stream metering pump controls the flow rate of the molten liquid. The molten extrudates are simultaneously draw-down by winders through a spinneret and air-cooled into fibers 10 to 50 micrometers in diameter. The main process variables for melt-spinning are the extrusion temperature, mass throughput, take-up velocity, and cooling temperature

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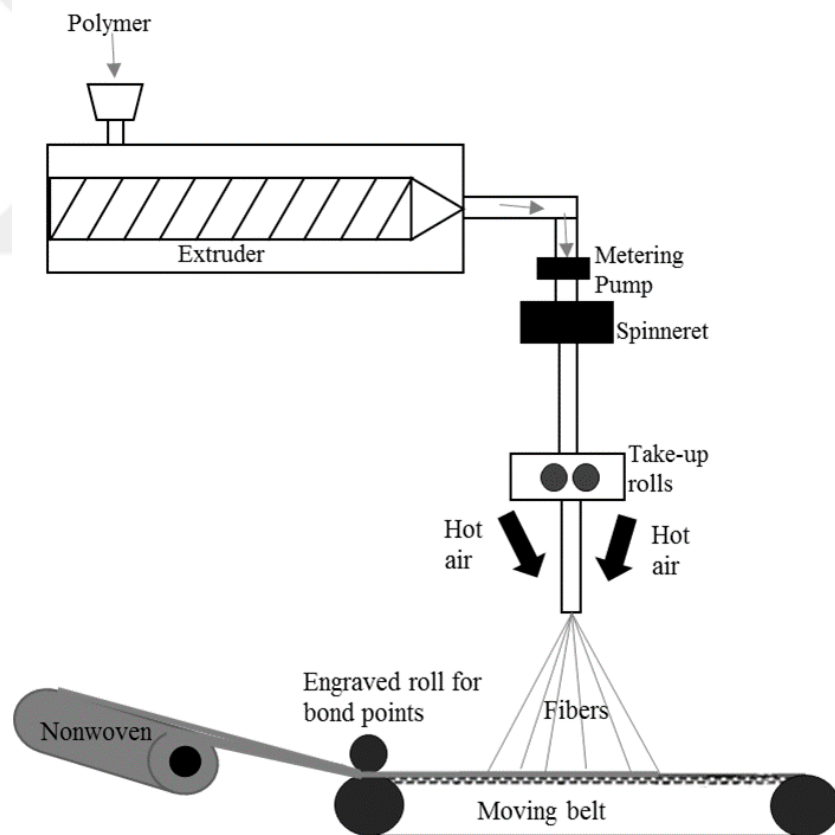


Figure 3. Schematic of a typical process for melt-spinning of polymers followed by production of nonwoven fabrics. Schematic diagram of a melt-blowing process

Nonwoven fabrics are structures that consist of fibers entangled together chemically, mechanically, or thermally. Thermally bonding processing is called ‘spun-bond’ technique (spun-laid, spun-melt blown). Industrial nonwovens are produced in a rapid, continuous process immediately after fiber spinning with several groups of spinnerets used to produce large-amount of fibers. As-spun fibers are blown by hot air onto a moving belt where they form a web by thermal bonding, as depicted in the lower part of the schematic in Figure 3. Number of bond points and their areal density, coupled with web thickness, influences nonwoven properties¹⁶. The strength of nonwovens is typically much smaller than that of woven fabrics, but nonwovens are produced at a speed almost an order of magnitude faster than that of woven counterparts, which makes them very inexpensive.

1.3 Biodegradable Materials

1.3.1 Poly-(lactic acid)

Because of environmental problems associated with synthetic polymers, bio-based materials have gained a great deal of importance. Polyesters, which can be degraded by hydrolysis (without any chemicals or enzymes) have started to emerge as key players in the biodegradable polymer industry. Poly-(lactic acid) (PLA) is one such biodegradable polyester that is a linear aliphatic thermoplastic, which is polymerized from lactic acid monomer (2-hydroxypropionic acid), as displayed in Figure 4 (a) . Lactic acid is obtained by the fermentation of bio-based, carbohydrate-rich sources¹⁷. The carbon source for lactic acid fermentation can be either in pure sugar form such as glucose/sucrose or sugar-containing products such as sugar cane, potato, corn, or wheat^{18,19}.

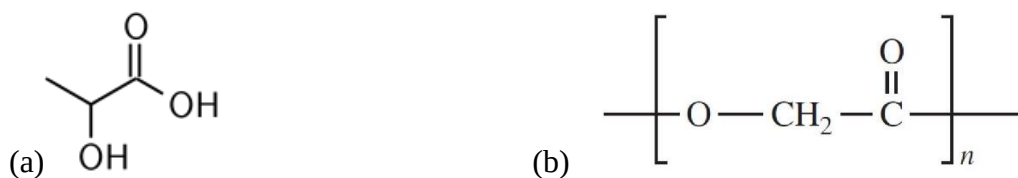


Figure 4. Chemical structure of (a) lactic acid and (b) poly-(lactic acid)

PLA is an environmental-friendly plastic that is biodegradable, compostable, and recyclable. Its properties are comparable to petroleum-based polymers such as polyethylene, polypropylene, polyethylene terephthalate (PET), and polystyrene (PS). However, it is an expensive material (4.80 \$/kg) compared to the petroleum-based polymers.

Poly-(lactic acid) possesses good mechanical properties, thermal processability, stability and can be processed by injection molding, film extrusion, blow molding, thermoforming, fiber-spinning, and film-forming. PLA properties depend on its molecular weight, thermal history, processing methods, and moisture content. Its bulk properties are compared with those of PE and PP in Table 1 (adapted from references ^{18,20-24}). PLA has a melting temperature of about 175 °C, and crystallinity of about 37%. Both amorphous and crystalline polylactides show brittle behavior at room temperature. PLA is starting to be used in disposable products, biomedical materials, textiles, and food packaging.

Advantages of PLA over PE and PP can be summarized as:

- PLA is produced from renewable sources;
- It is compostable like natural fibers; and

- It is possible to reuse PLA for corn, beets, rice growth.

Table 1. Comparison of mechanical and thermal properties of PLA, PP, and PE

	PLA	PP	PE
Density (g/cm³)	1.25-1.29	0.90-0.91	0.91-0.97
Tensile strength (MPa)	16-150	21-37	10-40
Tensile Modulus (GPa)	0.4-4.1	1.0-2.1	0.14-0.40
Tensile elongation (%)	2.5-100	200-600	400-700
Melting temperature (°C)	173-178	160-171	110-150

Unfortunately, there are also several disadvantages of PLA. One of the major disadvantages to its use in high-volume products is its relatively high cost (\$5 /kg) compared to its non-degradable petroleum-based counterparts (\$1/kg). Also, while neat PLA is biodegradable, its degradation rate is quite slow. One way to reduce the cost and improve the biodegradation rate is to blend PLA with inexpensive agricultural bio-fillers, which are discussed next.

1.3.2 Soy-based fillers

Millions of soybean bushels are produced annually because soybeans are an excellent source of protein, carbohydrate, and oil. Over 3 tons of soybean meal is left after a ton of oil is extracted. The effort of American soybean farmers and processors has been to find innovative uses for this side-stream. One of them is to use soy as agricultural filler in polymer matrices, so it is important to understand the characteristics of soy ²⁵.

Soybeans belong to the Leguminosae (legumes) family ²⁶. Figure 5 (adapted from reference ²⁷) shows the schematics of typical soy production with the major products being soymeal and soy oil. Others components are soy stem, leaves, pods, and soy hulls. Soybeans are cracked and dehulled after cleaning and drying. Soy-hulls are by-products that contain mostly carbohydrates and fibers used in animal feed ²⁸. Defatted soybean flakes (containing less than 1.5% oil) are produced after the dehulled soybean is conditioned, rolled into flakes, and oil is extracted from the flakes by addition of hexane. De-solventizer is applied to the flakes to obtain food-grade soy production and helps the hexane removal from the defatted soy flakes.

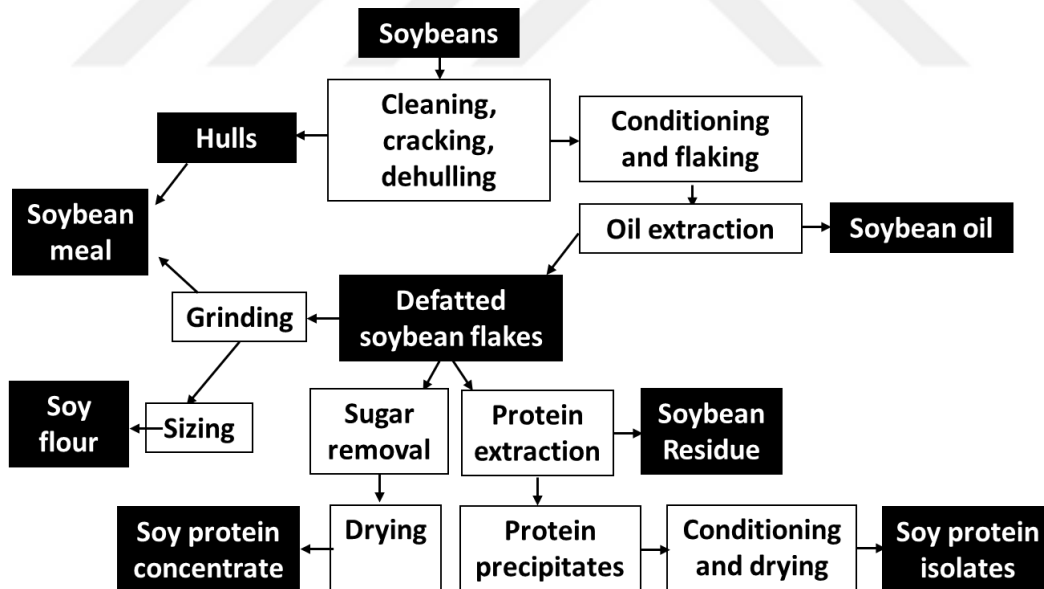


Figure 5. Soy production schematics

The main components of soybean on a dry basis are proteins (45 wt%), carbohydrates (35 wt%), oil (20 wt%), and moisture (variable). It also contains minerals (iron, copper, manganese, calcium, magnesium, zinc, cobalt, and potassium), vitamins (thiamin and riboflavin), and phosphorus ²⁹.

Proteins are linear biopolymers made of amino-acids. Twenty amino acids serve as monomeric units for proteins, with each amino acid having a unique R group. The amine group of one amino acid and a carboxylic acid group of another amino acid are bonded to each other via peptide bonds to form proteins (Figure 6). In synthetic polymers, an equivalent amide bond and a water molecule are formed by the reaction of an acid and amine group ³⁰.

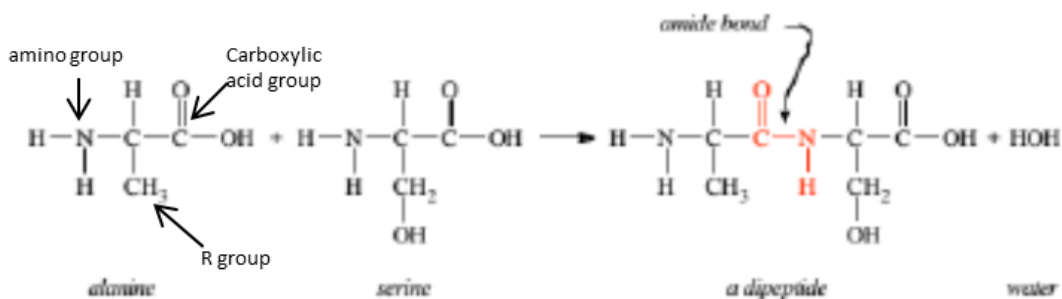
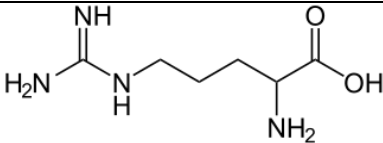
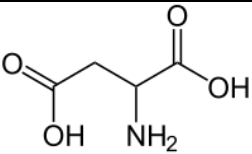
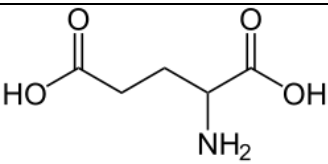


Figure 6. Formation of a peptide bond by the linkage of two amino acids via polycondensation (adapted from Reference ³⁰)

Predominant amino acids in soy proteins are globulins, arginines, and aspartic acids. They consist of mainly acidic amino acids (aspartic acid and glutamic acid), non-polar amino acids (alanine, valine, and leucine), basic amino acids (lysine and arginine), and non-polar amino acids (glycine) ³¹. Globulins, arginines and aspartic acids are hydrophilic; their chemical structures are shown in Table 2. The major globulin type found in soy protein is 7S. It consists of three major fractions: β -conglycinin, γ -conglycinin, and basic 7S globulin. 30-50% of whole seed protein is β -conglycinin that is a glycoprotein. Its ability to form hydrogen bonding imparts the hydrophilic property to this structure ³².

Table 2. Most important amino acids found in purified defatted soy protein

Amino Acid	Chemical Structure
Arginine ³³	
Aspartic Acid ³³	
Glutamic Acid ³³	

Carbohydrates are the next most abundant compounds (after proteins) in defatted soy. They are found in the form of simple sugars (Figure 7.a), oligosaccharides (Figure 7.b), and other polysaccharides. Soy carbohydrates have hydroxyl groups, so they have the property of water absorption and hydrogen bonding, which makes soy hydrophilic. In addition, most carbohydrates are soluble at a neutral pH, except insoluble fiber like cellulose (Figure 7.c) ³⁴.

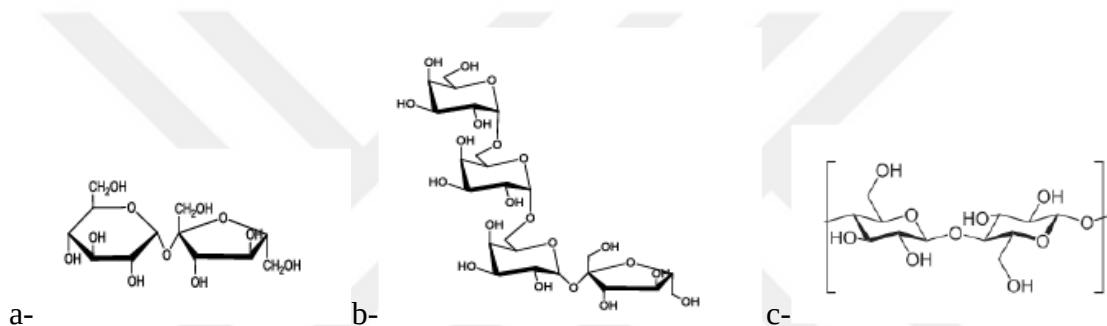


Figure 7 (a) sucrose (a simple sugar), (b) stachyose (oligosaccharide), (c) cellulose (found in insoluble fiber)

Various Soy Products

The most commonly used defatted soy products are soy flour, soy isolate, and soy concentrate. During soy flour processing, either a single- or double-screw extruder is used ³⁵. Soy flour is prepared by milling soy flakes through 100-, 150-, 200- or 325- mesh sieves ^{29,35}. Its protein content is around 56-59 w%, and carbohydrate content is 30-32 w%, as shown in Table 3 ³⁵. Its unit cost is 1.2\$ per kg.

Soy protein concentrates are made by the removal of most-soluble, non-protein ingredients from defatted soybean ^{29,35}. After extraction, they are ground into a powder

form. Its protein content is in the range of 62-72 wt% and sells for about \$3.5 per kg. Soy protein isolates are prepared after centrifugation of a significant amount of insoluble carbohydrates and extraction of soluble sugars by acid washing from defatted soybean ³¹. Among soy products, SPIs have the highest percentage of soy protein of more than 90 wt%. It is the least used soy product for food applications ^{29,35} and is quite expensive (above \$5 per kg).

Table 3. Composition of soy products: soy flour, concentrate and isolate

Constituents	Defatted soy flour	SPC	SPI
Protein	52-54	62-69	86-87
Fat	0.5-1.0	0.5-1.0	0.5-1.0
Crude fiber	2.5-3.5	3.4-4.8	0.1-0.2
Soluble fiber	2	2-5	<0.2
Insoluble fiber	16	13-18	<0.2
Ash	5.0-6.0	3.8-6.2	3.8-4.8
Moisture	6-8	4-6	4-6
Carbohydrates	30-32	19-21	3-4

In its neat form, soy does not have any fiber-forming ability, and the bulk material does not possess any ductility. Nonetheless, its abundance led to its industrial use starting in the 1940s at the Ford Motor Company for car upholstery³⁶. However, the fibers were brittle and disintegrated quickly in the wet state. Thus, soy was chemically modified and mixed with plasticizers (water, glycerol, sorbitol, sodium chloride, zinc chloride) to

improve its spinnability. However, the fibers were still brittle, and other mechanical properties were poor for nonwoven applications³⁷⁻³⁹.

1.4 Soy-filled Polymer Composites

By using the advantage provided by composites, soy has been incorporated into synthetic polymer matrices to form materials with significantly high ductility than that found in pure/neat soy. The concept of using such inexpensive bio-based fillers into synthetic polymers also serve the purpose of reducing the dependence on synthetic polymers, such as non-biodegradable polyolefins. This route leads to the production of environmental-friendly materials possessing an acceptable level of mechanical properties.

ASTM standards define ‘bio-based materials’ as that containing “carbon-based compound(s) in which the carbon comes from contemporary (non-fossil) biological sources.” Further, according to ASTM D7075, ‘bio-based product’ is defined as “a product generated by blending or assembling bio-based materials, either exclusively or in combination with non-bio-based materials, in which the bio-based material is present as a quantifiable portion of the total product mass of the product.”⁴⁰. In other words, a composite can be called as ‘biocomposite’ if one of the components of a composite is bio-based. Bio-based fillers are available in particulate or fiber form that is obtained from plant seeds, stems, fruits, leaves. The examples for commonly used fillers are cellulose, hemicelluloses, wood⁴¹, pectin, lignin, flax seed, rice^{42,43}, and soybean.

Fillers have been used in various materials to lower material costs. Particulate fillers, which are materials in powder-state with a maximum size of 100 μm , are added to

polymers to reduce cost and improve/modify properties. Density, material cost, optical properties, thermal/electrical conductivities, thermal expansion, mechanical properties, biodegradation rate, and morphology are some of the properties that can be modified by fillers. The incorporation of solid particulates into polymer matrices typically deteriorates the flow characteristics of the composite melt because of increased viscosity. The shear viscosity is dependent on the amount of filler, filler shape, and size, nature of polymer and filler^{44,45}. Particulates tend to form agglomerates during composite processing, which results in deterioration of properties.

With regards to tensile properties, particulate composites typically possess a higher modulus but lower strength, as compared with neat polymer. For instance, polypropylene composites reinforced with glass-beads display a lower tensile strength of 15 MPa as compared to 25 MPa for neat PP at 20 vol%⁴⁶. In contrast, the tensile modulus increased from 1000 to 1500 MPa by the incorporation of glass-beads⁴⁶. Overall, these composite properties depend on volume fraction of the filler, as well as filler and matrix properties.

Soy protein has received significant attention in research studies due to its abundance, low cost, and degradability. However, as noted earlier, soy protein has poor ductility. Addition of glycerol or methyl glucoside to soy protein makes it more flexible and processible due to the weakening interactions between protein molecules^{47,48}. Due to the poor properties of pure soy products, soy can be used as a filler within polymer matrices.

1.4.1 Blends of soy and polyethylene

There have been several published studies on soy filled polyethylene composites. Most of them concentrated on the process improvement by either processing technique or using compatibilizers/ plasticizers. Jeevananda et al.⁴⁹ compounded LLDPE (99 wt%) and soy protein isolate (1 wt%) using a twin-screw extruder using a temperature profile of 156-180°C. The compounded polymer was then blown into films by a single-screw extruder at a temperature range of 170-190°C. These LLDPE-blown films containing 1 wt% SPI were reported to have a tensile strength (TS) of 14 MPa and elongation at break of 144% where the neat LLDPE films displayed a TS of 27 MPa and elongation at break of 157%. This decrease is the result of the weakening intermolecular bonding of the polymer network.

Sam et al.⁵⁰ increased the filler content and used a compatibilizer to improve the properties of the composites. Soy-LLDPE blends were first blended in a batch mixer and compression-molded at 150°C for 10 min under a laboratory-scale press. Polyethylene-grafted maleic anhydride (MAPE) was used as a compatibilizer. The blends were prepared at the soy concentrations of 5, 10, 15, 20, 30, 40 wt%. The mixing torque of soy-LLDPE showed that the blend without MAPE had higher stabilization torque than that of the one with MAPE. The reduction in energy consumption during processing means that the compatibilizer improved the flow characteristics of the blends.

Sam et al.⁵⁰ also found that incorporation of soy caused a reduction in tensile strength and elongation at break. The tensile strength of LLDPE was reported as 24 MPa and decreased to 13 MPa at 5 wt% soy loading, and 2 MPa at 40 wt% soy loading. This

much decrease was because of the agglomerations of soy in LLDPE, and lack of compatibility between filler and polymer matrix. The composites had higher Young's modulus (450 MPa for 40 wt% soy) than that of neat LLDPE (180 MPa), which was explained by the stiffening effect of the powder. MAPE improved all the tensile properties of the composites as compared to those of uncompatibilized ones, by improved interfacial adhesion. Thermal analysis showed that melting temperature decreased after soy inclusion into LLDPE. The crystallinity increased by the compatibilizer. Thermal stability of the blends decreased with soy inclusion, but MAPE improved the thermal stability.

The same research group, Sam et al.⁵¹, used another compatibilizer, epoxidized natural rubber (ENR), for soy-LLDPE blends, and the blends were exposed to electron-beam irradiation. ENR as compatibilizer improved tensile strength, tensile modulus, and elongation-at-break by improving soy dispersion by chemical interaction. However, even the ENR compatibilized composites have poorer tensile properties, like MAPE compatibilized composites, than that of the neat LLDPE.

Instead of using a compatibilizer, Iyer and Torkelson⁵² tried to find a new processing technique to get better soy dispersion in PE and better mechanical properties for soy-LLDPE composites. They blended LDPE with 5–40 wt % soy flour by melt mixing (MM), single-step solid-state shear pulverization (SSSP), and two-step single-screw extrusion processes followed by solid-state shear pulverization (SSE-SSSP) at a temperature of 130°C. The two-step single-screw extrusion process followed by solid-state shear pulverization involves first pelletizing of soy flour-LLDPE blend via single-screw

extrusion, then melt-mixing and powdering of these composite pellets. The powder was further compression-molded. An improved soy flour dispersion was obtained on the composites made by two-step SSSP compared to those made by MM or single-step SSSP.

According to Iyer and Torkelson⁵², well-dispersed soy flour led to an increase in the composite's tensile modulus where the moduli were measured at 270 MPa, 200 MPa and 160 MPa for the composites containing 20 wt % soy flour and 80% LDPE made by SPE-SSPE, MM and SSSP respectively, where LDPE had a tensile modulus of 155 MPa. The composites were found to have less tensile strengths than that of neat LDPE. Even the good filler dispersion resulted in a decreased strength. Elongation-at-break in all the composites was reduced relative to that of neat LDPE (500%). The elongation-at-break values for composites containing 20 wt % soy flour and 80% LDPE made by SPE-SSPE, MM and SSSP were measured at 70%, 7%, and 14%, respectively. For all soy flour contents, the composites produced by SSE-SSSP showed better mechanical properties than those made by MM and SSSP. For 40 wt% soy flour content, all composites showed brittle behavior. SF-LDPE blend showed a similar rheological behavior compared to that of neat LDPE.

Another method, film extrusion, was used by Thellen et al.⁵³ to process soy-polyethylene blends. LLDPE was blended with three different soy flour groups having average diameters of 8, 11, and 22 μm . The extrudates were prepared by a twin-screw extruder at 140°C at a soy flour loading level of 10 and 20 wt%. These extrudates were pelletized, and further melt-drawn through a single screw extruder into 150 μm thick

monolayer films. For improved properties of the films, multilayer films were produced through three-layer film coextrusion that included two single-screw extruders connected to a feed-block and a film die. Films were produced with an average thickness of 65 μm . The temperature profile of the extruders was at 190 $^{\circ}\text{C}$ for extruder 1, 155 $^{\circ}\text{C}$ for the extruder 2, 160 $^{\circ}\text{C}$ for the feed-block and die.

Thellen et al.⁵³ reported that the monolayer soy-LLDPE composite films demonstrated higher yield stresses than neat LLDPE film, so soy flour behaved as a reinforcing agent. Soy flour with the particle size of 11 μm yielded in composite multilayer films with the highest yield stress. The elongation at break values of all film sets was not statistically different from each other.

By increasing soy flour size and content, moisture sensitivity of the monolayer films increased, and the contact angle of the films decreased⁵³. This means that soy flour contributed to the improved film hydrophilicity. Also, they found that the samples containing the larger size soy particles have higher hydrophilic properties in the short-term, but similar long-term moisture absorption. The purpose of multilayer film coextrusion was to create films with enhanced moisture protection by covering hydrophilic soy flour in the middle with LLDPE. The multilayer films with 20 wt% soy content were found to be more hydrophilic than the films containing 10 wt% soy flour. Elongation-at-break values were decreased with increasing soy content. Soy flour addition resulted in a 38% decrease in the oxygen permeability of the LLDPE multilayer films but did not affect water vapor permeability. These films are proposed to be used in flexible food packaging applications.

1.4.2 Blends of soy and polypropylene

Like the studies on soy-PE blends, those on soy-PP followed a similar route by enhancing the processability of the composites by the addition of various compatibilizers/plasticizers. Sailaja et al.⁵⁴ blended PP with 20, 30, 40, 50 wt% soy flour by melt mixing at 210°C, and then molded these blends into composites. Glycerol was used as a plasticizer. Maleic anhydride-grafted polypropylene (MAPP) was used as a compatibilizer at the concentrations of 6% and 9 wt% to improve the processability of the soy flour-PP blend.

Sailaja et al.⁵⁴ also found that the impact strength of the blends reduced as the soy flour content increased. Both glycerol and MAPP contributed to increasing the impact strength of the composites as compared to that of the uncompatibilized ones at lower soy flour concentrations. The use of glycerol improved tensile strength, modulus, and ductility of soy-PP composites. The use of MAPP improved the tensile modulus but had a negative impact on tensile strength, impact strength, and elongation at break. In addition, thermal aging was accelerated as the soy flour content increased. Thermal degradation studies showed that the compatibilized blends were less thermally stable than uncompatibilized blends.

In addition to organic compatibilizers, inorganic ones have also been reported in the literature. Guettler et al.^{55,56} studied the effect of potassium permanganate autoclave treatment on the mechanical properties and the contact angles of soy/PP composites prepared by injection molding. Soy hulls (SH), soy flour, and soy protein isolate were used

as soy fillers. Soy fillers were subjected to autoclave treatment. Potassium permanganate was mixed with soy fillers at 1:2 mass ratio. MAPP was blended into the soy-PP mixture as coupling agents at 2.5 wt%. A single-screw extruder was used for melt-mixing of the soy (30 wt%) and PP at 190°C. The extruded blend was pelletized, and mixed with the coupling agent in a twin-screw extruder. Then, the samples were prepared by injection molding at 190°C. These samples were annealed in an oven for 15 min.

The inclusion of maleic anhydride to SF-PP blends improved the impact strength for the composites with the autoclaved fillers but decreased for the composites having potassium permanganate. Guettler et al.^{55,56} explained this with the higher hydrophilicity of autoclaved SF, and also lower hydrophilicity of soy flour coupled with potassium permanganate. The impact strengths of SPI composites were affected more than that of SH composites by these treatments because of the high protein content of SPI. Potassium permanganate treatment increased the water contact angle of the soy composites (from 57° to 69° for SF, from 64° to 86° for SPI) except that with SH, and reduced the polar surface energy of soy-PP composites except that with SH. Autoclave treatment did not have any impact on the water contact angles of SF and SH composites but increased for SPI composites from 64° to 49°. It increased the polar surface energy of soy-PP composites except that with SF. Soy hulls and SPI were found to be the most appropriate soy material based on the polar surface energy characteristics.

Instead of using a compatibilizer, Iyer and Torkelson⁵² also used SSE-SSSP technique to produce soy-PP composites as discussed earlier for soy-LDPE composite

processing. The aim was to get good soy flour dispersion in PP and good mechanical properties without any compatibilizer. A processing temperature of 180°C was used. Adequate dispersion and adhesion of SF in the PP matrix was achieved by this processing technique. The composite's tensile modulus where the moduli were measured at 1400 MPa, 950 MPa and 900 MPa for the composites loaded by 20 wt % soy flour and 80% PP made by SPE-SSPE, MM and SSSP respectively, where PP had a tensile modulus of 1050 MPa⁵². Tensile strength displayed a similar trend for LDPE composites. As the soy content increased, the tensile strength of the composites decreased. It was reported at 29 MPa for 20 wt % soy flour and 80% PP composite where neat PP showed a strength of 33 MPa. Elongation-at-break in all the composites was sharply reduced relative to that of neat LDPE (700%). The elongation-at-break values were measured at 6%, 3% and 4% for the composites loaded by 20 wt % soy flour and 80% PP made by SPE-SSPE, MM and SSSP respectively. Even 5 wt% soy flour loading resulted in a very low ductility of 15 %.

Thermal analysis showed that soy flour degraded significantly in the air at temperatures close to PP processing temperatures. SF-PP blend had better thermal stability than neat PP. This was due to the char formation from well-dispersed SF that acted as an oxygen barrier and reduced degradation⁵².

1.4.3 Blends of soy and poly-(lactic acid)

Some of the earliest studies on soy-PLA blends were reported by Zhang et al.⁵⁷ in 2006. SPC and SPI were used as filler types, and poly(2-ethyl-2-oxazoline)(PEOX) was used as a compatibilizer. The compounds were blended in a twin-screw extruder with

soy:PLA ratio of 30:70, 50:50, 70:30 (wt/wt) and compatibilizer content of 1-5 wt% at 160°C. The extrudates were injection-molded.

The soy-PLA blends had higher viscosities than neat PLA viscosity. At low frequency (0.1 rad/s) and 5% strain, the viscosity of SPC-PLA and SPI-PLA (30:70) were measured at 6×10^5 Pa.s and 2×10^6 Pa.s, respectively, while PLA has a viscosity of 8×10^4 Pa.s. At higher concentrations, the rheology experiments could not be done properly because of the high viscosity and poor flow of the blends. SPI-PLA was found to have a higher viscosity than that of SPC-PLA. It was proposed that due to the lower protein content and higher carbohydrate content of SPC than SPI, the compatibility between SPC and PLA was better than that between SPI and PLA. High viscosity resulted by SPI ended up with the composites having clear phase separations⁵⁷.

PEOX improved soy dispersion inside PLA, so the tensile strength, elongation-at-break, and water resistance of SPI-PLA and SPC-PLA blends improved. The property improvements due to the compatibilizer were by a larger extent for SPI-PLA than SPC-PLA. Thermal analysis showed that PLA in the blends showed a higher melting enthalpy than neat PLA (12.7 J/g for PLA vs. ~30 J/g for soy-PLA); thus, PLA crystallization was induced and accelerated by soy filler. PLA in the blends showed slightly lower glass transition temperature than that of neat PLA (59.3°C)⁵⁷.

The effect of methylene diphenyl diisocyanate (MDI) and sodium bisulfate (NaHSO₃) on mechanical, thermal, and water absorption properties were reported by Fang et al.⁵⁸. SPI-PLA blends containing NaHSO₃ and MDI were mixed in an intensive mixer

at 175°C for 4 min, and the samples were compression-molded. Both NaHSO₃ and MDI improved the compatibility between SPI and PLA, so the tensile strength of the blends increased by 32% for the samples compatibilized with only NaHSO₃ and 81% for ones compatibilized with both NaHSO₃ and MDI. SPI and MDI had no effect on the ultimate water absorption.

Fang et al.⁵⁸ also showed that PLA did not show any crystallization peak while SPI-PLA blends had an obvious crystallization and double-melting peaks during thermal analysis. This behavior is the same as the reported result by Zhang et al.⁵⁷ showing that SPI behaved as a heterogeneous nucleating agent for PLA, and accelerated PLA crystallization. The double melting peak was interpreted as the simultaneous occurrence of melting-reorganization and recrystallization-remelting of the lamellae that formed originally during crystallization. Glass transition temperature of SPI-PLA blend was decreased by the addition of the compatibilizers, as the compatibility between filler and polymer increased. The mobility of the PLA macromolecular segment was restricted due to the increased interaction of PLA with SPI in the presence of the compatibilizers, and this caused an increase in T_g. A similar study was done with SF-MDI-PLA composites (20:0.5:99.5 wt%)⁵⁹. Similar results as for SPI-MDI-PLA blends were observed for PLA composites filled with soy flour.

Synergetic effect of dual compatibilizers of PEOX and MDI in the properties of SPC-PLA (30:70 wt%) composites were reported by Liu et al.⁶⁰. The raw materials were first compounded in a twin-screw extruder at 155°C, and then the blends were injection-

molded at 165°C. The addition of dual compatibilizers enhanced the interfacial adhesion between two phases. The tensile strength of these compatibilized composites had 6% higher tensile strength than that of neat PLA. The tensile modulus was slightly higher than that of neat PLA while elongation-at-break was slightly lower than that of neat PLA.

Liu et al.⁶¹ plasticized these SPC-PLA blends with water and glycerol, and NaHSO₃ was used as a compatibilizer. Phase separations were observed for the blends plasticized with glycerol. Water led to better SPC dispersion in the matrix and better mechanical properties. Water and glycerol did not make any contribution to the blend crystallization.

In order to improve soy protein processing with polymers, compatibilizers have been used. Lubricant effect on soy-PLA composite properties was investigated by Liu et al.⁶². They proposed that lubricants would be better than plasticizers for soy-PLA processing because of the negative effects of plasticizer on melt viscosity, glass transition temperature, and melting point. Thus, they studied the effect of acetyl tri-n-butyl citrate and alkene bis fatty amide as processing aid on SPC-PLA composites. Acetyl tri-n-butyl citrate behaved as a plasticizer by decreasing glass transition and melting temperatures and increasing PLA crystallinity. Alkene bis fatty amide functioned as a lubricant after it reached saturation point in PLA melt at a low concentration. At a higher concentration than the lubricant's saturation concentration, the crystallinity decreased. This is due to the increased size of SPC particles by the lubricant coverage. Both helped to reduce the melt

viscosity and improved processing. Both resulted in lower mechanical properties. Further, using the same lubricants, SPC-PLA blends were extruded into foams⁶³.

Calabria et al.⁶⁴ used triacetin as a plasticizer to produce SPI-PLA blends for slow-release-fertilizer systems. A fertilizer was used in the blends. In this case, the SPI matrix (60 wt%) was filled with PLA at 40 wt%, and the blends were injection-molded. The samples showed a porous morphology. The samples with fertilizer degraded slower in the soil. Yang et al.⁶⁵ investigated adipic anhydride as a plasticizing agent on soy-PLA blends and found better mechanical properties and morphology in the plasticized blends compared to that of uncompatibilized ones. Soy with adipic anhydride accelerated the biodegradation of PLA.

Maleic anhydride (MA) grafted PLA was used as a compatibilizer to improve the processability and the properties of SPC-PLA (30:70) injection-molded samples. Zhu et al.⁶⁶ reported better mechanical properties were achieved in the presence of MA-grafted PLA due to the enhanced interfacial adhesion.

Film processing of soy-PLA has been reported by Gonzalez and Igarzabal⁶⁷. Cast films with a thickness of 50 μm were produced containing up to 60 wt% SPI. Glycerol was used as a plasticizer. At high SPI content, the biodegradation rate of the blends was higher. SPI improved the opacity of the films, which is important for food packaging.

1.5 Objectives

The literature studies reviewed above indicate that a considerable effort has been devoted to the injection and compression molding of soy-based polymer composites to obtain low-cost and environmentally friendly products. The aim of most prior studies has been to improve the processability of soy-filled polymers. For this reason, different compatibilizers/plasticizers/lubricants and different compounding methods have been investigated. However, the blends have not been thoroughly investigated for their properties as fibers⁵³. Also, the spinnability of soy-polymer blends and the resulting fiber properties have not been thoroughly investigated. As discussed before, polymer melt-spinning has its own advantages over other spinning methods, and soy is a bio-based product that is economical and environmentally-friendly. Therefore, the primary goal of this research was to process soy-filled polymers into bio-based fibers via melt-spinning for potential applications in disposable nonwovens. Specifically, this dissertation is aimed at assessing the melt-spinnability and properties of fibers produced from soy flour filled in following polymers:

- (i) LLDPE matrix, which has the lowest possible processing temperature among synthetic thermoplastic polymers;
- (ii) PP, which is the most widely used synthetic polymer for nonwovens; and
- (iii) PLA, which is a biodegradable polymer, but is expensive and has a slow rate of degradation in its neat form.

The organization of the remaining dissertation is as follows. **Chapter 2** presents results for various soy flour contents, thermal processing conditions, and flow characteristics of soy flour-filled LLDPE using rheological and thermal analysis. Mechanical properties and moisture absorption of the fibers are reported. FTIR analysis was used to investigate polymer and filler relation with compatibilizer. The bulk of the results presented in this chapter are based on our published paper⁶⁸.

Chapter 3 presents results for fibers based on PP matrix, the most common polymer in the disposable market. Processing time of the blends was estimated from isothermal degradation studies for better particle dispersion. The effect of soy flour composition on mechanical properties was investigated. Hydrophilicity, washing, and coloring properties, which are desired properties for textile applications, were assessed.

Chapter 4 presents results on a biodegradable polymer matrix, PLA, that was used to produce fibers filled with soy flour. The processing temperature of the blends was established. Morphology and mechanical properties of the fibers were investigated. The soy filler effect on hydrolytic degradation characteristics is reported.

Finally, **Chapter 5** summarizes the major conclusions drawn from this research. It also provides recommendations for future studies.

CHAPTER 2

SOY-FILLED POLYETHYLENE FIBERS FOR MODIFIED SURFACE AND HYDROPHILIC CHARACTERISTICS

2.1 Introduction

As reviewed in Chapter 1, there is a growing interest in using bio-based products due to their environmental sustainability⁶⁹. Environmentally-friendly fibers are needed for the preparation of inexpensive textiles used in disposable non-wovens. Polyethylene (PE), one of the most widely used synthetic polymer in the world, is an easily processible, flexible, and recyclable material ⁷⁰. PE is a thermoplastic polymer used mostly in the packaging industry but has also been used on a limited basis in the non-woven textile market, which is dominated by polypropylene (PP). However, PE is easier to process than PP and has been gaining price advantage (over PP) from the recently developed ethylene feedstocks, such as shale gas and bio-based sugar fermentation routes ⁷¹⁻⁷⁴. The processing temperature of PE is about 40⁰C less than that of PP and leads to energy saving during the processing step ⁷⁰. Therefore, this chapter is aimed at the potential use of PE in large-volume, disposable non-wovens, that will have a less environmental impact than neat PE.

Fibers made of neat PE have been used for spun-bond hygiene products, twine construction, ropes, filtration fabrics, blinds, awnings, and other outdoor and automotive fabrics ^{70,75,76}. PE can be blended with bio-based materials, such as starch ⁷⁷⁻⁷⁹, wheat ^{80,81}, cellulose ^{82,83}, and lignin ⁸⁴. Soy flour has also been incorporated into PE and other polymers in films and bulk composite forms ^{85,86}. Soy flour, which contains 36%–56%

protein and up to 35% carbohydrates, is a renewable, inexpensive material which can be used as a bio-based filler in polyolefin matrices^{33,53}. Literature studies indicate that some of the polysaccharides^{87,88} that have been incorporated into polyolefin matrices behave as component of the blend and not merely as fillers. The dispersion and property enhancements in soy flour/ PP/linear low-density PE (LLDPE) composites were reported by Iyer and Torkelson⁵². The LDPE and PP composites with 5–40 wt % soy flour were produced by single-screw, motor-and-cup, and two-step single-screw extrusion processes followed by solid state shear pulverization. Soy particle dispersion inside polymer resin was improved by two-step process which led to an increase in the composite's tensile modulus and strength, but the composites were brittle (low strain-to-failure of 6%) at 20 wt % soy flour.

The chemical incompatibility between hydrophilic bio-materials and hydrophobic polyolefins is a major challenge for producing ductile composites because the bond between these components is weak^{24,89}. Therefore, the use of compatibilizers is beneficial to enhance interactions between polymers and fillers to make the product more flexible and processible⁸⁴. In the literature, compatibilizers, such as glycerol, maleic anhydride, or dimethyldiethoxysilane have been reported to improve the interfacial adhesion between soy flour and matrix, and hence the mechanical properties^{50,54,90}. For instance, Sailaja et al.⁵⁴ reported that 6 wt % glycerol added as a compatibilizer into soy flour/PP blend during melt mixing enhanced soy particle dispersion and the adhesion between filler and matrix. Sam et al.⁵⁰ processed soy powder/PE composites grafted by maleic anhydride produced by batch melt mixing. They reported about 75% increase in Young's modulus, 45%

increase in tensile strength, but 20% decrease in elongation-at-break, by using a composition containing 5 wt % compatibilizer. In addition to organic compatibilizers, inorganic ones have also been reported in the literature. The effect of potassium permanganate on the mechanical properties of soy/PP/homopolymer–PP copolymer composites prepared by injection molding indicate ⁵⁶ improved the compatibility of soy with polymer matrix, so the toughness and strength of the composite increased.

In contrast to hydrophobic PE, hydrophilic soy has a tendency to absorb significant moisture, which can be a problem for producing bulk, industrial composites. However, when used as fibers or fabrics, the presence of hydrophilic soy may have an advantage (over neat PE) because such partially hydrophilic fibers are comfortable to wear. Prior studies have reported that sheets produced from pure soy protein absorbed water and led to a weight gain of 75 wt % ²⁴. Thellen et al. ⁵³ found that the water absorption of the composite soy/PE thin film increased with increasing soy content.

In summary, prior studies show that soy flour has been used as a filler in polyolefin to produce bulk composites, but thin fibers made of PE/soy flour have not been systematically reported in the literature. Soy-based hydrophilic polyolefin fibers can be of value in non-woven fabrics because of their ease of processing, eco-friendliness (reduction of synthetic polymer content), and cost competitiveness. However, their mechanical, microstructural, and hydrophilic properties need to be investigated. Therefore, the overall goal of this research was to study the spinnability of soy flour filled fibers with LLDPE as the continuous phase and monoglyceride as a compatibilizer. Specific objectives of this research were to: (i) measure flow characteristics of various soy/LLDPE blends to

determine suitable compositions for continuous spinning, (ii) study the microstructure and mechanical properties of the resulting fibers, and (iii) characterize the moisture absorption properties of the soy/LLDPE fibers.

2.2 Experimental

2.2.1 Materials

A fiber grade LLDPE (Dow Aspun 6835A) with a melt flow index of 17 g/10 min and a density of 0.95 g/cm³ was used. Defatted soy flour used throughout this study was obtained from Archer Daniels Midland Company (Decatur, IL), and had a nominal composition (all in wt %) of 53% protein, 30% carbohydrate, 9% moisture, 3% fat, and remainder dietary fiber.

The soy flour was ground by the producer to a fine size, with an average particle size of 3.4 μm . Dimodan distilled monoglyceride (DuPont) was used as a compatibilizer. Soy flour (S) and monoglyceride (M) were dried in a vacuum oven for 2 h at 80⁰C (~100 kPa vacuum).

2.2.2 Processing

To determine a spinnable composition, four different blends were prepared with compositions listed in Table 4. Soy flour was added to LLDPE at 20 and 40 wt % content. Following the determination of spinnability of these compositions, the next step was using monoglyceride as a compatibilizing agent. Soy flour and monoglyceride were physically mixed in a 1:1 (S50/ M50) or 3:1 (S77/M23) weight ratio. The ratio of soy to

monoglyceride was determined based on literature values and preliminary studies. Next, LLDPE pellets were mixed with S or S/M mixtures to obtain about 15 g of the mixture. The mixture was fed into a 15 mL twin-screw extruder (DSM Xplore, Geleen, the Netherlands) for melt compounding. The blends were compounded in the speed controlled and recirculation mode at a rotation speed of 100 rpm and a recirculation time of 5 min. The temperatures were set to 145⁰C in the feed zone and to 140⁰C in the extruder and die.

Table 4. Various compositions (wt %) of soy (S)/monoglyceride (M)/ LLDPE blends used in this study

	S	M	LLDPE
S40/PE60	40	0	60
S20/PE80	20	0	80
S20/M20/PE60	20	20	60
S23/M7/PE70	23	7	70
S77/PE23	77	23	0

The viscosities of the blends were measured at low shear rates using the ARES rheometer (TA Instruments, New Castle, DE) with a cone-plate fixture of 25 mm diameter and a cone angle of 0.1 rad. Viscosity at high shear rates was measured by a capillary rheometer (ACER2000, Rheometric Scientific, Piscataway, NJ), with both tests performed at 140⁰C.

The fibers were produced by melt spinning of neat LLDPE and S/M/LLDPE blends using DSM twin-screw extruder. A custom-designed 3-hole spinneret having capillary

diameters of 0.5 mm was attached at the end of the extruder. Fiber spinning was carried out in the force-controlled mode. Fibers were obtained by air-cooling during the fiber draw-down step. As control samples, neat LLDPE fibers were spun using similar conditions as those used for soy-based fibers. To obtain experimental/prototype samples of nonwoven fabrics, S/M/LLDPE fibers were compacted in a hydraulic Carver press at 1350 kg and 120 °C for 1 minute using textured metallic plates. Both fibers and nonwovens were stored in ziplock bags at ambient temperature prior to testing.

Static tensile tests were conducted following the ASTM D2256 procedure with an initial sample length of 2.5 cm. Mechanical testing of the fibers was performed at a cross-head speed of 0.25 cm/min with a 22 N load cell (ATS 900, Applied Test Systems, Butler, PA). Fiber diameters were measured using an optical microscope (Olympus BX60 Optical Co., Tokyo, Japan) with nine measurements obtained along the length and then averaged. The microscope was also used to measure the soy agglomerate size in the blend fibers. Image-Pro image analysis software was used to calculate the nominal diameter. Scanning electron microscopy (SEM) was used to assess the microstructure and morphology of cryogenically fractured fibers by examining the cross section and lateral surfaces (Hitachi S-4800, Hitachi, Japan).

Thermogravimetric analysis (TGA) of soy flour (S), monoglyceride (M), LLDPE, S/M mixture, and S/M/PE blends was conducted using a Pyris1 instrument (Perkin Elmer, Waltham, MA). The samples were heated in an aluminum pan under air atmosphere from 25 to 500 °C at a heating rate of 10 °C/min. Fourier transform infrared (FTIR) spectroscopy was conducted in the attenuated total reflectance mode using a Thermo Nicolet 6700 FTIR

spectrometer (Thermo Scientific, Madison, WI). Spectra for S23/M7/PE70 and LLDPE fibers, soy flour, and monoglyceride were obtained in a spectral range of 4000 down to 400 cm⁻¹ wavenumbers.

The contact angle between water and 23S/7M/70PE blend (and LLDPE as control) was measured using films prepared by compression molding (Carver hydraulic press, Fred S. Carver Inc., NJ) at 120⁰C and 20 kN compaction force. A contact angle goniometer (Kruss, Model DSA10, Hamburg, Germany) was used in conjunction with the sessile drop technique. The static contact angle measurements were obtained with distilled water at a static time of 30 s.

For moisture absorption in 23S/7M/70PE fibers, samples were dried for 4 h at 80⁰C in a vacuum oven (~100 kPa vacuum). Approximately 1 g of fibers was exposed to steam for 1 h. The fibers were periodically removed from the steam environment, wiped using Kim-wipes, and dried with a blow-drier for 20 s to remove the free/excess water left on the fiber surface. After weighing, the fibers were placed again in the steam environment for subsequent tests. After absorption studies, fibers were again dried and their weight loss measured.

2.3 Results and Discussion

2.3.1 Viscosity and Fiber Spinning

For fiber spinning, viscosity is an important characteristic of the material. Highly viscous materials are difficult to extrude, whereas very low melt elasticity results in spinning difficulties⁹¹⁻⁹³. The first blend consisted of 40 soy and 60 wt % LLDPE, and had

a viscosity 50% higher than that of pure LLDPE, as shown in Figure 8. The large soy content led to limited drawdown as the blended melt had poor melt strength. Large amounts of soy flour (immiscible solid) introduce significant amounts of weak solid/liquid interfaces. During draw-down, extensional stresses lead to failure at these weak interfaces and result in reduced melt strength. The presence of large soy amounts also increases the shear viscosity of the blend as the agglomerates reduce the ability of the polymer chains to flow past each other⁹⁴. In prior studies, Iyer and Torkelson⁵² produced S/LDPE composites through a single screw extruder by using a maximum soy content of 40 wt %, and they were fairly brittle. However, these were only extruded, but not drawn-down.

Next, a blend containing smaller content of soy was investigated, and the viscosity of S20/PE80 was found to be lower than the S40/PE60 blend, and close to that of pure LLDPE. The morphology of the S20/PE80 blends is shown in Figure 9(a), where the brown and white colors in the optical micrograph represent soy agglomerates and LLDPE, respectively. The blend had poor particle dispersion and large agglomerates with nominal diameters of $150 \pm 107 \mu\text{m}$ were observed as compared to the diameter of single soy particle of $3.4 \pm 1.7 \mu\text{m}$. Neither the agglomerate size nor dispersion was uniform. The fiber drawdown was limited with large visible soy particles on the fiber surface. S20/PE80 blend could only be spun into coarse fibers with a large diameter of $85 \pm 40 \mu\text{m}$. The rheological and morphological characteristics of this composition were comparable with those of S/LDPE blend reported by Iyer and Torkelson⁵².

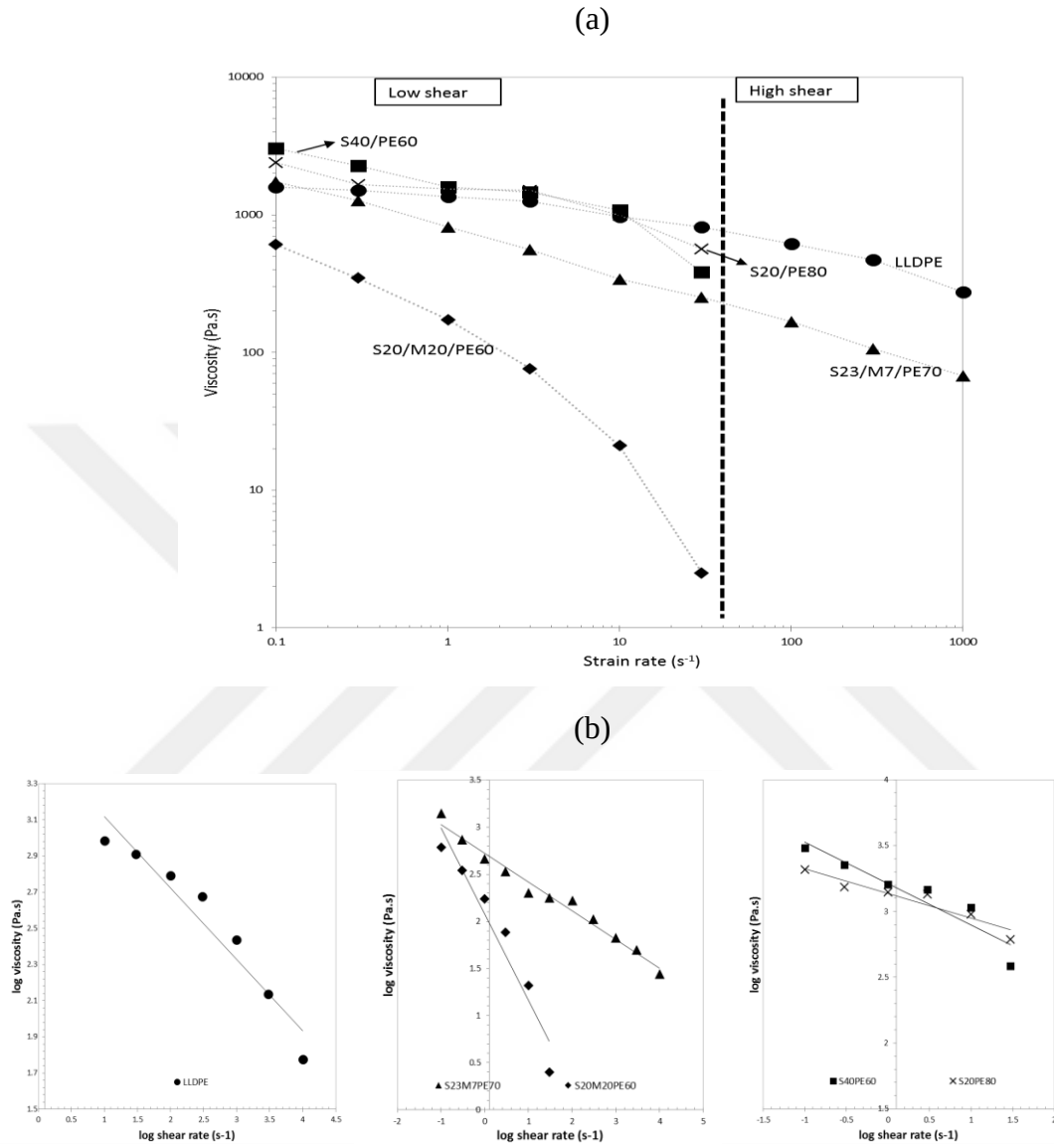


Figure 8. Shear viscosity of soy (S)/PE blends having different compositions: ■ S40/PE60, S20/PE80, ♦ S20/M20/PE60, ▲ S23/M7/PE70, ● pure LLDPE. The tests were conducted at 140°C. Low-shear experiments were performed using a cone-and-plate rheometer, whereas high-shear measurements were done using a capillary rheometer (a) experimental results (b) Linear least squares fit for each blend on log-log scale.

The power-law model parameters for various compositions are listed in Table 5. Polymeric melts behave as shear thinning fluids, with power law exponent $n < 1$ ⁹³. S20/M20/PE60 is an extremely shear thinning with a power law exponent of 0.17 compared to 0.74 for pure LLDPE. The highly shear thinning feature of this blend was caused by the large amount of M in the blend with possible migration out of the melt. Also, fiber spinning of S20/M20/PE60 blend was problematic due to excessive compatibilizer, which likely coated the extruder screw and limited the feeding and metering of the material through the extruder.

Table 5. Power-law viscosity parameters, n and K , for various soy/LLDPE blends

Sample	n	K (Pa.s ^{n})
S40/PE60	0.70	2130
S20/PE80	0.77	1312
S20/M20/PE60	0.17	212
S23/M7/PE70	0.65	810
LLDPE	0.74	1402

Therefore, the compatibilizer content was reduced to 7 wt %, and a composition S23/M7/PE70 was investigated next. Viscosity of this S23/M7/PE70 blend was measured as 1971 Pa.s at a low shear rate of 0.1 s^{-1} , which decreased to 288 Pa.s at 10 s^{-1} . The high shear experiments showed that the blend was shear thinning with a power law exponent of 0.65. The viscosity of S23/M7/PE70 blend at high shear rates was lower than that of pure PE, but overall the flow characteristics of S23/M7/PE70 resemble that of LLDPE.

Optical micrographs of S23/M7/PE70 are displayed in Figure 9(b). As noted earlier, the S20/PE80 blend (i.e., without compatibilizer) displayed poor dispersion of soy in the LLDPE melt/matrix and contained large agglomerates. In contrast, soy agglomerates observed in S23/M7/PE70 fibers were much smaller, nominally $32 \pm 14 \mu\text{m}$. It is evident that the presence of monoglyceride improved the dispersion of soy in LLDPE matrix.

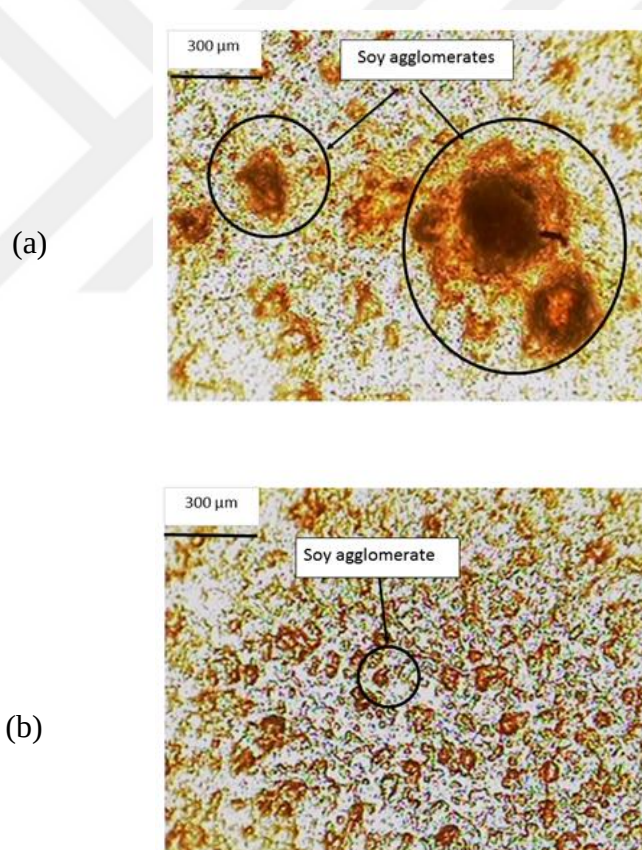


Figure 9. Optical micrographs of (a) soy(S)/LLDPE blend containing 20 wt% S and 80 wt% LLDPE (i.e., no monoglyceride M) (b) soy-monoglyceride-LLDPE blend containing 23 wt% S , 7 wt% M, and 70 wt% LLDPE

Figure 10 presents schematics of possible interactions between soy and LLDPE. Without a compatibilizer, the hydrophilic soy particles prefer to stay in the proximity of other soy particles to generate large agglomerates. In contrast, when monoglyceride is added, its hydrophilic “heads” can cover soy particles, as also illustrated in Figure 10. Polar interactions can favorably occur between amine and hydroxyl groups of soy flour and carboxyl group of monoglyceride ⁵⁴.

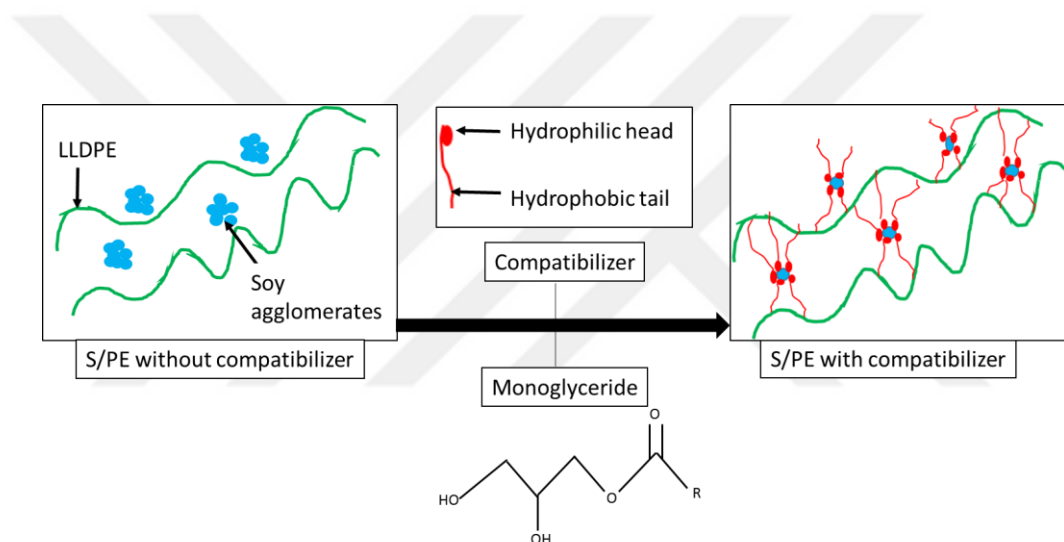


Figure 10. LEFT: A schematic illustrating the segregation and agglomeration of soy particles (hydrophilic) within polyethylene (hydrophobic) in the absence of a compatibilizer; RIGHT: physical interactions between hydrophilic soy and monoglyceride “head”, and hydrophobic LLDPE and monoglyceride tail, leading to enhanced dispersion of soy particles

To verify the nature of these interactions, FTIR spectroscopy was conducted on pure components (soy, monoglyceride, and LLDPE) and S23/M7/PE70 fibers, and various

spectra are displayed in Figure 11. The soy flour spectrum consists of a broad band at 3307 cm^{-1} attributable to O-H and N-H groups from the proteins and moisture. The protein component of soy flour is also represented by 1630 cm^{-1} peak that represents the amide I band (C=O) stretching in the protein secondary structure. The main absorption bands from the carbohydrates are between 1200 and 1000 cm^{-1} arising from C-O, C-C, and C-O-H stretching as well as C-O-H bending⁹⁵⁻⁹⁷.

The monoglyceride spectrum is also characterized by a broad band at 3300 cm^{-1} (similar to soy) in addition to two strong peaks at 3000–2850 cm^{-1} from C-H vibrations and 1715 cm^{-1} due to the carbonyl (C=O) of the ester group. For LLDPE, major peaks include C-H stretching at 2910 and 2844 cm^{-1} , and C-H bending at 1460 cm^{-1} . Also, included next is a numerically superposed spectrum combining spectra of pure components, which shows no significant difference with peaks observed for actual S23/M7/PE70 fibers. The absence of any new/major chemical functionality in S23/M7/PE70 fibers indicates that no significant chemical reaction occurred in the soy-PE blends during melt processing, and that the interactions are primarily physical in nature.

Having established that 23 wt % S, 7 wt % M, and 70 wt % LLDPE was well-suited for melt processing, continuous fiber spinning was successfully performed, and a small spool of these fibers is displayed in Figure 12. The fibers were quite thin and flexible, with a nominal fiber diameter of $45 \pm 11 \mu\text{m}$. Figure 13 displays SEM micrographs for lateral and cross-sectional surfaces of these fibers. Fibers obtained from neat LLDPE have a smooth lateral surface and cross-section, as shown in Figure 13(a).

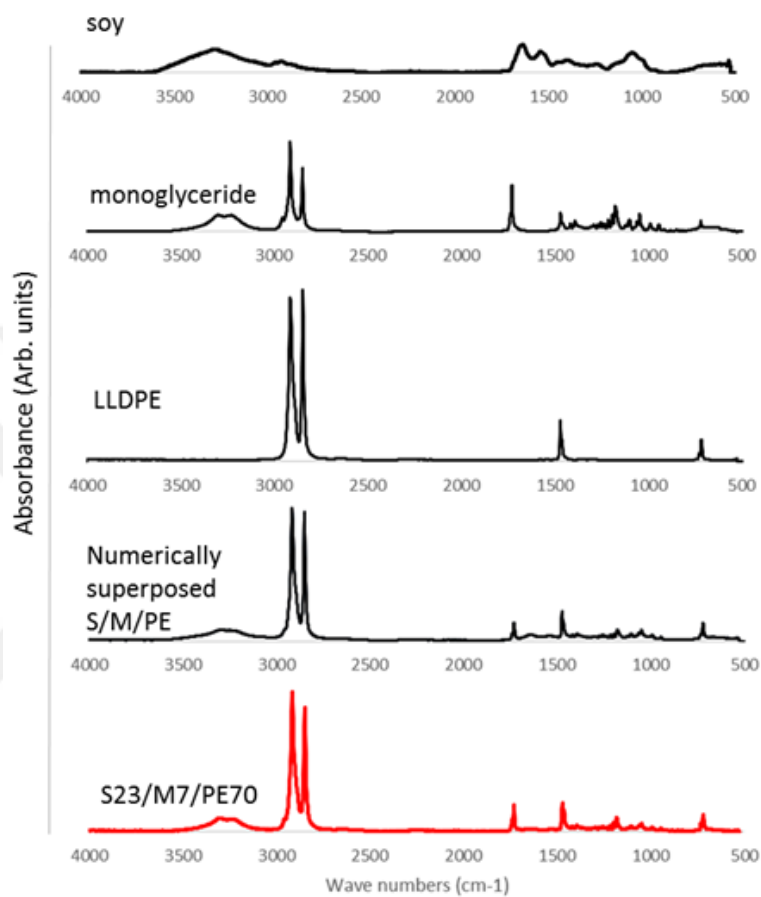


Figure 11. FTIR spectra of pure components soy, monoglyceride, LLDPE, a superposition of all three pure component spectra, and a spectrum of actual soy-PE fiber (S23/M7/PE70).



Figure 12. A small roll of soy-PE fibers continuously spun fibers from an S23/M7/PE70 composition

In contrast, S23/M7/PE70 fibers have a rough surface because of the presence of small soy agglomerates on the fiber surface, as shown in Figure 13(b). The roughness of the lateral surface influences the tactile feel of fibers. LLDPE fibers have a plastic-like tactile “hand” that is not highly desirable for nonwoven fibers. Rough surface and texture provides cotton-like characteristics to the soy-PE fibers and improves their tactile properties ⁹⁸.

Soy agglomerates are also evident in the fiber cross-section of S23/M7/PE70, as displayed in Figure 13(c). However, the size of these agglomerates is much smaller than that observed for the uncompatibilized blend. The small holes on the surface of the fibers are likely due to the soy agglomerate stuck on the other half of the fiber during cryo-fracturing. Previous studies by Sailalaja et al.⁵⁴ reported micrographs of uncompatibilized soy/PP composite surfaces with holes about 100 μm , indicating large agglomerates due to

inadequate dispersion in the absence of a compatibilizer. When glycerol was added as a compatibilizer in their study, the hole size (also agglomerate size) reduced to nominally 50 μm , indicating that the reduction of the agglomerate size observed here is generally consistent with prior literature results.

In an attempt to further enhance the degree of dispersion, melt compounding experiments were also conducted at temperatures higher than 140–145 $^{\circ}\text{C}$, which was used to obtain fibers reported above. However, the soy-PE melt turned progressively darker as melt temperatures exceeded 150 $^{\circ}\text{C}$, and the fibers were of poor quality. To verify the degradation characteristics as a function of temperature, TGA was conducted on various pure components and blends, and thermograms are presented in Figure 14. Neat LLDPE displays the most stable response, with no measurable weight loss till 350 $^{\circ}\text{C}$. In contrast, soy (S) displays the least stable response, with a steady rate of weight loss observed starting from 50 $^{\circ}\text{C}$ itself and extending till 150 $^{\circ}\text{C}$, a quasi-stable response then till 200 $^{\circ}\text{C}$, and a significant degradation beyond 250 $^{\circ}\text{C}$. Monoglyceride (M) displays a fairly stable behavior till about 100 $^{\circ}\text{C}$, a very small rate of weight loss till about 200 $^{\circ}\text{C}$, and then a drastic weight loss above 250 $^{\circ}\text{C}$.

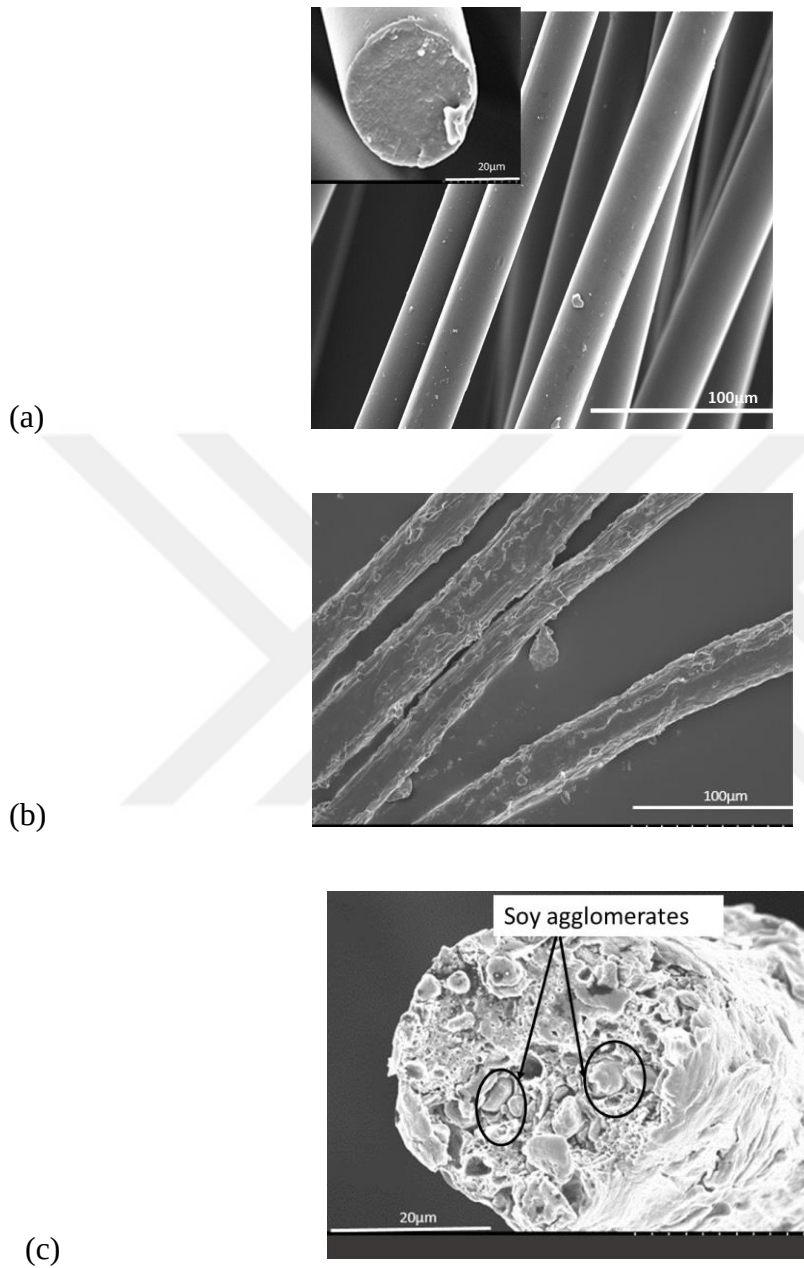


Figure 13. SEM micrographs of (a) the smooth lateral surface of LLDPE control fibers with the inset showing the cross-section of a LLDPE fiber (b) lateral surface of S23/M7/PE70 soy-PE fibers, and (c) cross-section of a 23S/7M/70PE fiber

It is noted that degradation characteristics much above 150⁰C are not relevant as the primary purpose of these TGA experiments was to ascertain melt stability of the bio-based compositions, and will not be discussed further. For soy-monoglyceride mixture (S77/M23), the addition of more stable M to S, helps the S/M blend retain a slightly more stable response till about 150⁰C. Further addition of the most stable LLDPE to S/M mixtures further improves the stability, although a small loss is still observed at 150⁰C. It is noted that weight loss poses problems during melt processing because of significant volume increase (two orders of magnitude) as solids convert to gases. Overall, these TGA results confirm that 140–145⁰C is a practical upper limit of stability for melt processing of these soy-monoglyceride- PE blends.

2.3.2 Mechanical Properties

The mechanical properties of various fibers are listed in Table 6. LLDPE control fibers were measured to have a tensile modulus of 952±85 MPa and a tensile strength of 42.8±5.0 MPa, consistent with typical properties of LLDPE reported in the literature (700–900 MPa for tensile modulus, and 20–250 MPa for tensile strength)⁹⁹⁻¹⁰¹. For S20/PE80 fibers, the tensile modulus and strength were 655±80 and 16.9±1.7 MPa, respectively. Compared with the ones for pure LLDPE fibers, all mechanical properties of S20/PE80 fibers reduced significantly due to inadequate dispersion and large size of soy agglomerates in the fiber, as shown in the optical micrograph [Figure 9 (a)]. The agglomerates themselves are very weak as they have voids among soy particles. Also, the interphase between soy flour and LLDPE is not well-formed without the presence of a compatibilizer.

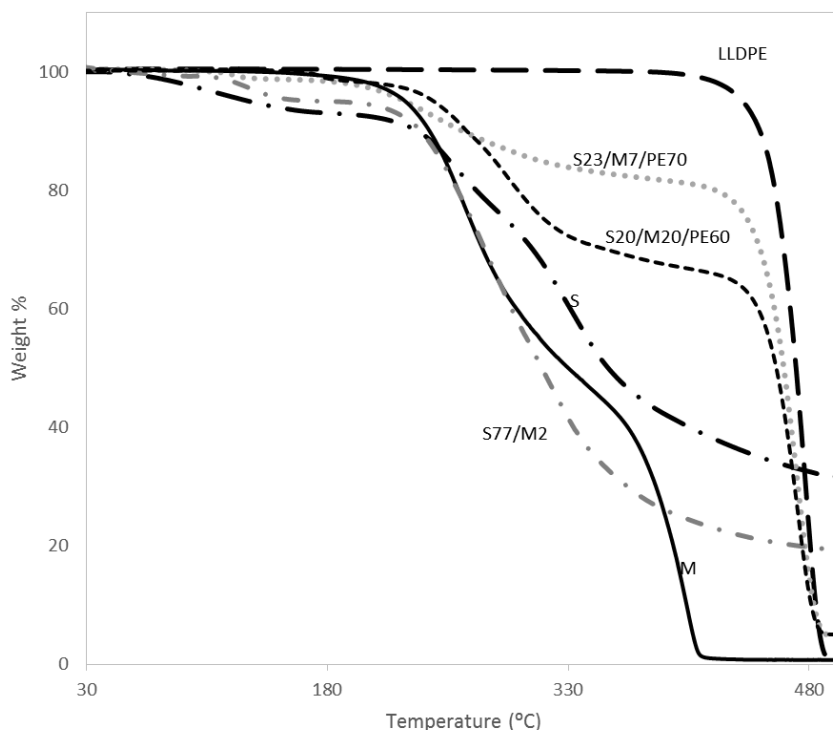


Figure 14. Thermogravimetric analysis of monoglyceride (M), soy flour (S), LLDPE (PE), and blends containing (wt%) S77/M23, S20/M20/PE60, S23/M7/PE70

Fibers produced from S20/M20/PE60 blend (i.e., containing compatibilizer) were measured to have a tensile modulus of 620 ± 91 MPa, which is about 35% less than that of LLDPE, with no major change in strength as compared with that of pure LLDPE. However, this composition had excessive compatibilizer, which caused inefficient spinning as noted earlier. For S23/M7/PE70 fibers, the tensile modulus and strength were 615 ± 38 and 57 ± 8 MPa, respectively. S23/M7/PE70 fibers had 35% lower modulus than that of neat LLDPE fibers. Although lower modulus is not desired for primary structural applications, this

lower modulus (stiffness) provides a softer feel to fibers, which is actually desired for textile use.

Table 6. Summary of mechanical properties of soy-filled and neat LLDPE (control) fibers

Fibers	Tensile Modulus (MPa)	Yield Stress (MPa)	Yield Strain (%)	Failure Strength (MPa)	Strain to Failure (%)
LLDPE	952 ±85	25.0±2.7	5.7±1	42.8 ±5.0	512±50
S20/PE80	655 ± 80	16.9±1.7	4.0±0.2	18.5±3.1	90±31
S20/M20/PE60	620±91	18.5±1.3	7.0±1.3	34.3 ±5.0	251±24
S23/M7/PE70	615±38	15.0±1.0	4.5±0.5	57.0±8.0	280±29

The stress-strain curves of S/PE fibers are displayed in Figure 15. All fibers displayed elastic and plastic regions. The elastic deformation is reversible and is fully recovered when the load is removed. The initial response is the elastic region and the slope of the curve gives Young's modulus. The stress-strain relationship in this regime follows Hooke's law, $\sigma = E\varepsilon$, where σ is stress, ε is strain, and E is Young's modulus. After this linear region, the yielding/plastic deformation begins and is irreversible. The yielding occurs at a nominally constant load, but increasing strain. As deformation continues, the fiber displays strain-hardening regime due to increased molecular orientation, which results in increasing stress until failure.

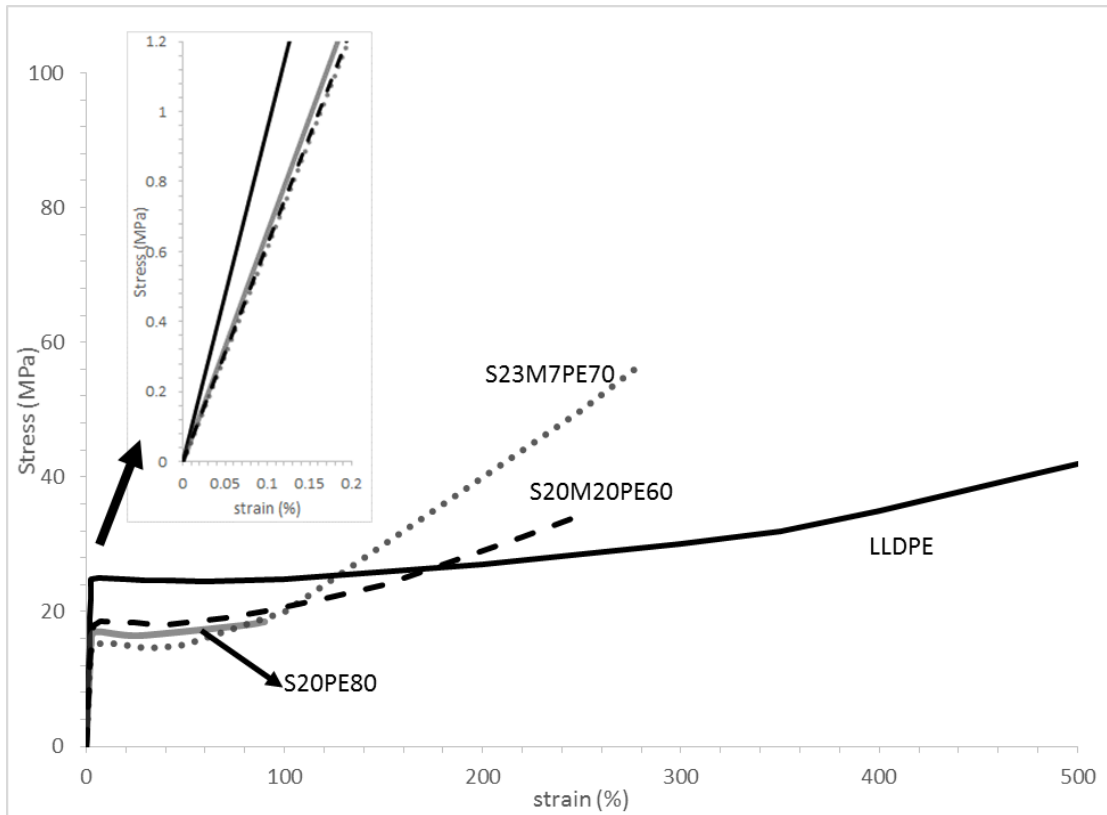


Figure 15. Stress-strain curves of pure LLDPE and biocomposite PE fibers containing: (i) 20 wt% soy (S) with no monoglyceride (M) (S20PE80), (ii) 20 wt% S, 20 wt% M and 60 wt% LLDPE (S20M20PE60), and (iii) 23 wt% S and 70 wt% LLDPE with 7 wt% M (S23M7PE70). The inset displays the stress-strain curves of the fibers in the elastic region showing clearly the slope of the curves.

2.3.3 Moisture Absorption

In addition to tensile properties, moisture absorption of fibers is also an important property of fibers especially when used in fabrics that can come into contact with human skin. Water contact angle (θ) values indicate the degree of hydrophilicity of a material, with a smaller angle indicating more hydrophilic behavior. Contact angles were measured for films prepared from S23/M7/PE70 to understand the effect of soy on LLDPE wettability. Representative images of droplets obtained after contact angle tests are shown in Figure 16. On S/M/PE surface, water droplet spread on the sample while one on LLDPE did not. Thus, the contact angle was measured at $95^{\circ} \pm 7^{\circ}$ for LLDPE control, and only $33^{\circ} \pm 4^{\circ}$ for S/M/PE. The large contact angle ($>90^{\circ}$) for LLDPE indicates a hydrophobic surface. The lower angle measured on S/M/PE surface revealed that soy particles on the surface improved the hydrophilicity of the blend because the contact angle is sensitive to the chemical composition of the external surface of the sample.

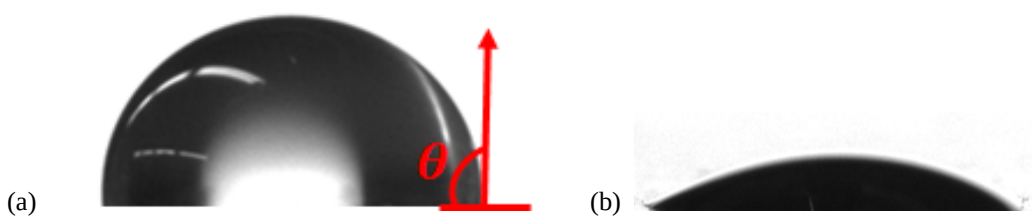


Figure 16. Representative images for water droplets obtained from contact angle measurement on: (a) neat LLDPE film, and (b) soy-PE film containing 23 wt% soy, 7 wt% monoglyceride and 70 wt% LLDPE

Water absorption experiments were also conducted to investigate the hydrophilic behavior of S23/M7/PE70 fibers. Figure 17 shows the water uptake as a function of exposure time of S/ M/PE and LLDPE (control) fibers to moisture. A small weight gain of 0.5% was measured for LLDPE control fibers. Given that actual water absorption inside LLDPE is negligible (in 1 h), this small measured value represents water that was trapped between the fibers even after the fibers were wiped and blow-dried. In contrast, S/M/PE fibers gained almost 20 wt % weight in 1 h. Due to the hydrophilic nature of soy, water absorption rate was high and equilibrated to about 20 wt % in approximately 1 h. This moisture absorption property is important for fibers/fabrics because it improves their comfort. Neat LLDPE fibers/fabrics can trigger a clingy (or sticky) sensation due to the lack of removal of moisture from the skin (perspiration)¹⁰².

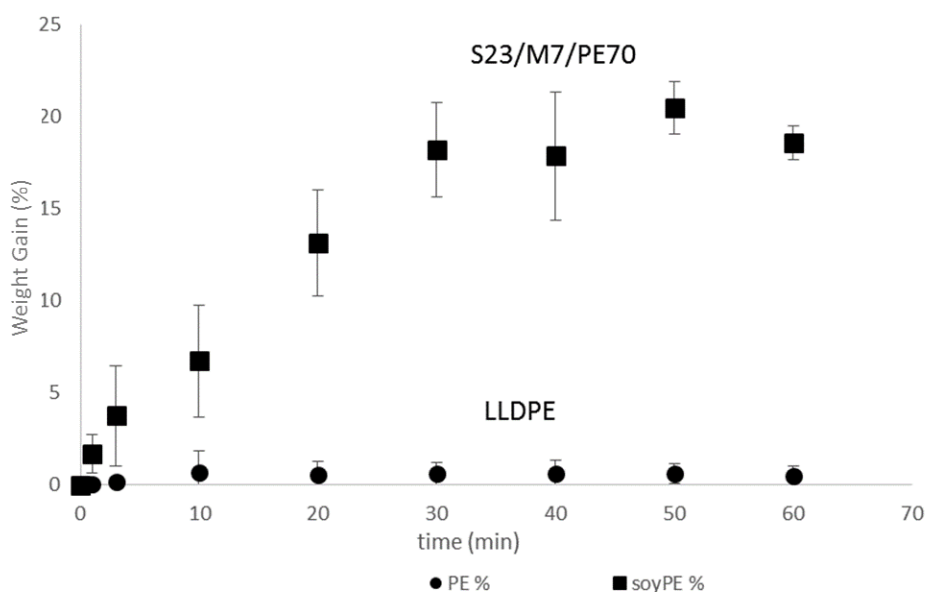


Figure 17. Moisture absorption in soy-PE fibers having S23/M7/PE70 composition. For comparison, data are also presented for LLDPE (control) fibers.

To determine if moisture led to any significant deterioration of fibers, their mass and tensile properties were measured after the fibers were dried. The weight loss was measured at 21.7 wt % of original mass for S/M/PE fibers indicating that about 1.7 wt% of soy flour was also lost (in addition to 20 wt % moisture) during the drying/handling steps. Their tensile modulus, yield stress and strain, strain-to-failure were measured at 597 ± 63 , 15.7 ± 0.6 MPa, $4.0\% \pm 0.8\%$, and $242\% \pm 47\%$, respectively. These properties were not significantly different from those of the unexposed fibers, but the tensile strength reduced by about 30% to 39 ± 3 MPa. A possible reason for the strength loss is that the swollen soy agglomerates caused some damage to the fibers, as seen from some cracks/splits displayed in Figure 18(b). The reduced strength of about 40 MPa is still an acceptable level for the use of such fibers in nonstructural applications like disposable nonwovens.

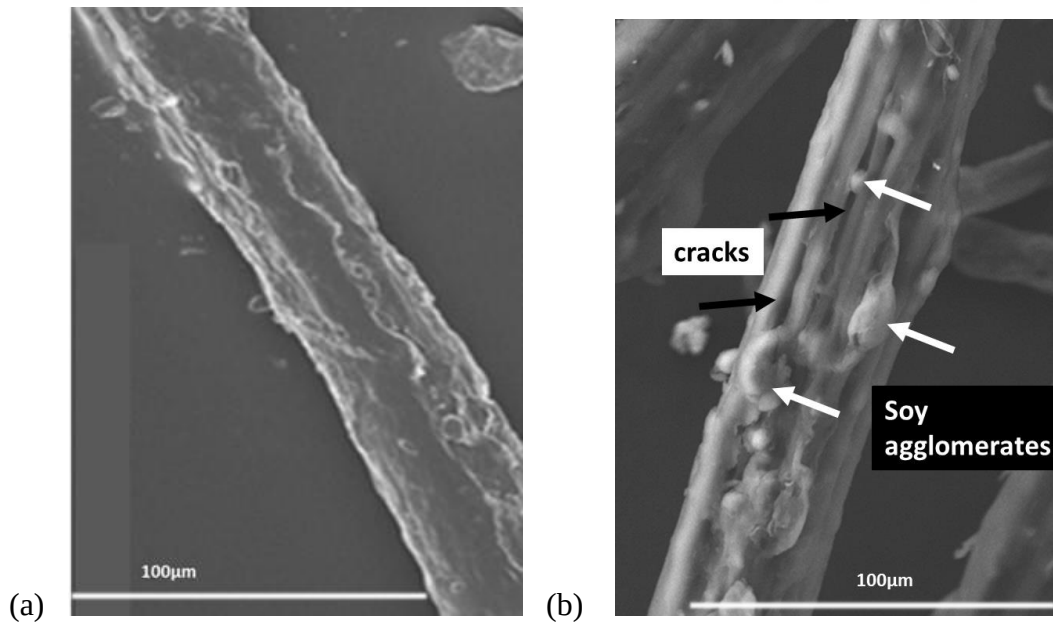


Figure 18. SEM micrographs of lateral surfaces of soy-PE fibers having S23/M7/PE70 composition: (a) as-processed fiber, and (b) fiber after exposure to moisture.

Finally, to assess the potential of soy-PE fibers for conversion into nonwoven fabrics, a limited quantity of soy-PE fibers were thermally compacted in a hydraulic Carver press using textured metallic plates. As shown in Figure 19, a prototype non-woven fabric sample was successfully obtained. Because surface fusion was still possible, soy-PE fibers could be converted into a non-woven fabric. This confirms the retention of thermoplastic characteristics of the composite fibers necessary for subsequent nonwoven fabric production.



Figure 19. An image of S23/M7/PE70 non-woven hot-pressed at 120°C for 1 min

2.4 Conclusions

This study establishes that soy/monoglyceride/polyethylene fibers can be produced by melt-spinning. Without a compatibilizer (monoglyceride), soy could not be adequately dispersed in LLDPE matrix. Soy/LLDPE blends compatibilized with monoglyceride (M) were found to be suitable for melt-processing, with 23 wt % soy, 7wt % M, and 70 wt %

LLDPE composition (S23/M7/PE70) showing a flow behavior similar to that of neat LLDPE. Although small agglomerates still existed, their presence on the surface actually provided the fibers with a tactile feel (“hand”) similar to that of natural fibers, that is, less plastic-like. S23/M7/PE70 fibers had a tensile modulus of 615 ± 38 MPa, about 35% less than that of pure LLDPE fibers. Lower modulus imparts softness to the fibers, which is desirable for textile use. Without a compatibilizer, the S/PE fibers were weak, but fibers containing 7 wt % compatibilizer possessed yield and tensile strengths of 15 ± 1 and 57 ± 8 MPa, respectively, that are adequate for potential use in disposable non-wovens. Contact angle measurements showed that S23/M7/PE70 fibers were generally hydrophilic with contact angles of about 34° (i.e., significantly less than 90°). In a hot, moist environment, these fibers gained about 20 wt % moisture in 1 h. These moisture-exposed S/M/PE fibers retained adequate tensile properties after moisture absorption and subsequent drying. The hydrophilic behavior, coupled with a desired tactile feel provided by the textured surface, indicates the potential use of the soy-PE fibers in disposable nonwovens.

CHAPTER 3

INFLUENCE OF SPINNING TEMPERATURE AND FILLER CONTENT ON THE PROPERTIES OF MELT-SPUN SOY FLOUR/ POLYPROPYLENE FIBERS

3.1 Introduction

In Chapter 2, it was established that soy flour filled polyethylene blends are spinnable into fibers. However, a majority of nonwovens are produced from PP, so this chapter discusses fibers produced by incorporating soy flour into PP matrix. It is noted that PP has to be processed in a temperature range of 165 to 250°C, which is much higher than that needed for PE and one where thermal degradation of soy can become a problem. However, as discussed in Chapter 1, melt-spinnability/processing of soy/PP fibers has not been systematically investigated in prior literature studies. Therefore, the objectives of the present study were to (i) identify melt-mixing and melt-spinning conditions for soy/PP fibers, (ii) determine the effect of soy content on the mechanical properties of soy-PP fibers and (iii) investigate the suitability of soy-PP fibers for disposable nonwovens in terms of moisture absorption and hydrophilic characteristics.

3.2 Experimental

3.2.1 Materials

Defatted soy flour, soy flour 7B, (53% protein, % 3 fat, % 30 carbohydrate, % 9 moisture, and %18 total dietary fiber) was obtained from Archer Daniels Midland. A fiber

grade PP, Dow 6D43 Resin, (melt flow index: 35 g/10min at 230°C, density: 0.9 g/cm³) was obtained in a pellet form. Dimodan distilled monoglyceride was used as a compatibilizer between soy flour and PP and purchased from Dupont. Soy flour and monoglyceride were dried in a vacuum oven for 2 hours at 80°C (~100 kPa vacuum).

3.2.2 Spinning

Soy flour and monoglyceride were manually mixed in 4:1 ratio on a weight basis chosen according to the previous studies^{68,103}. About 15 grams of the mixtures were prepared by physical mixing of polypropylene pellets at 70 wt%, 85 wt%, and 95 wt% with soy (SFM), and feeding to a 15 mL twin-screw extruder (DSM Xplore, Geleen, Netherlands). The blends were compounded in the speed-controlled and recirculation mode at a rotation speed of 100 rpm and mixed using a recirculation time of 2 min.

The blend containing 15 wt% SFM was used to conduct viscosity testing using an ARES rheometer (TA Instruments, New Castle, DE) equipped with a cone-plate fixture of 25 mm diameter and a cone angle of 0.1 rad. Shear viscosity was measured at four different temperatures: 160, 190, 220, and 250°C.

Fibers containing 15 wt% SFM (85 wt% PP) were also spun at melt temperatures of 160, 190, 220, and 250°C. These temperatures were selected based on PP fiber spinning temperature range (160-220°C) and also PP nonwoven processing temperature (~250°C). As shown in Figure 20, a custom-designed 3-hole spinneret with a capillary diameter of 500 µm was attached at the end of the extruder. Fiber spinning was carried out in the force-controlled mode at a force of approximately 3000 N. Fibers were obtained using a draw-

down ratio of approximately 100. SFM/PP fibers containing 70 wt% and 95 wt% PP were spun at only 190°C. The nomenclature of the fibers is summarized in Table 7. To obtain experimental/prototype samples of nonwoven fabrics, SFM/PP fibers were compacted in a hydraulic Carver press at 1350 kg and 125 °C for 1 minute using textured metallic plates. Both fibers and nonwovens were stored in ziplock bags prior to testing.

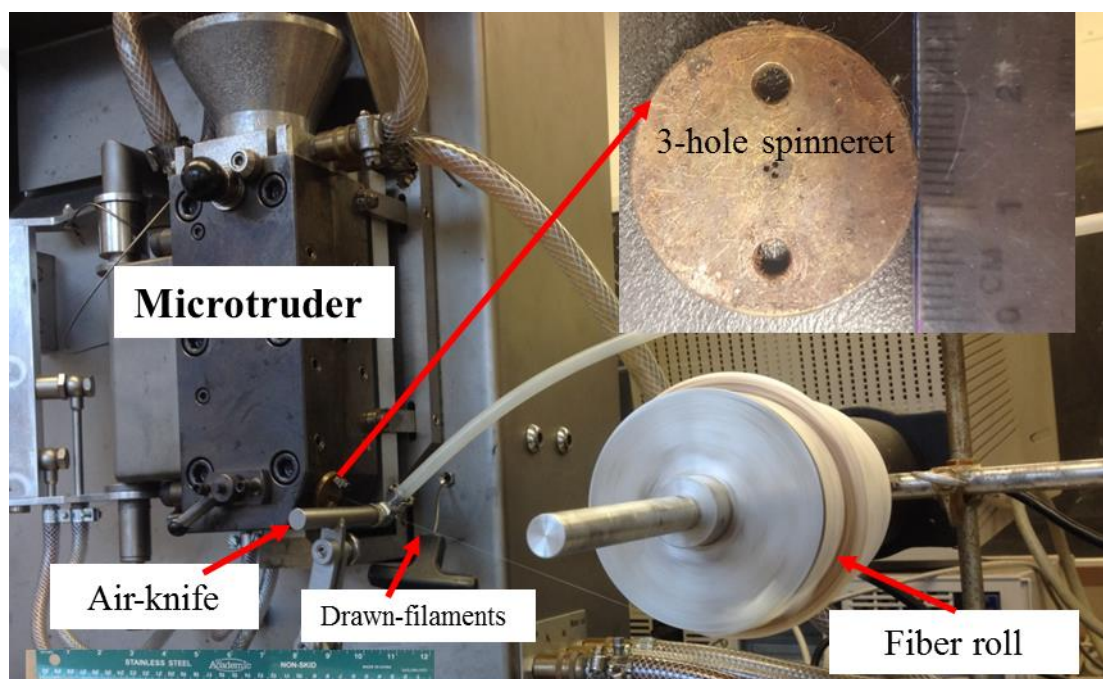


Figure 20. Spinning of SFM/PP fiber containing 5 wt% soy flour (SFM) and 95 wt% polypropylene using the DSM twin-screw extruder.

3.2.3 Characterization

Thermogravimetric analysis (TGA) was conducted using a TA instrument (TGA Q5000, TA Instruments, USA, USA). The SFM/PP blend was heated in an aluminum pan under the nitrogen atmosphere at a heating rate of 10°C/min. The temperature was

increased from 25°C to 160°C, 190, 220 and 250°C, as four separate experiments, and kept at those temperatures for 20 min.

Table 7. Compositions of the blends and spinning temperatures for various soy flour (SF), monoglyceride compatibilizer (M), and polypropylene (PP)

Fibers	SF+M (wt%)	SFM (wt%)	PP (wt%)	Spinning temperature (°C)
SFM5P95-190	4+1	5	95	190
SFM15P85-190	12+3	15	85	190
SFM30P70-190	24+6	30	70	190
SFM15P85-160	12+3	15	85	160
SFM15P85-220	12+3	15	85	220
SFM15P85-250	12+3	15	85	250

Scanning electron microscopy (SEM) was used to characterize the microstructure and morphology of the fibers (Hitachi S-4800, Hitachi, Japan). The fibers were fractured cryogenically to obtain cross-section images and sputter-coated with platinum to avoid charging. Optical microscopy (BX60; Olympus Corp., Lake Success, NY) was used to measure single fiber diameters.

Tensile tests were conducted following the ASTM D2256 procedure on single fibers, with an initial gage length of 2.54 cm. Mechanical testing of the fibers was performed at a cross-head speed of 0.25 cm/min with a 22 N load cell (Applied Test Systems Inc., Series 900). Five replicates were tested from each group.

The contact angle between water and SFM/PP blends was measured by pressing the blends into films at 160°C and 20 kN force (Carver hydraulic press). The test was performed using a contact angle goniometer (Kruss, Model DSA10) using a sessile drop technique. The static contact angle measurements were obtained with distilled water at a static time of 30 seconds.

Fibers containing SFM content of 0 (i.e., neat PP), 5, 15 and 30 wt% were dried for 4 hours at 80°C in a vacuum oven for moisture absorption studies. Approximately 1 g of fibers were exposed to moisture for 1 hour. The fibers were periodically removed from the steam environment, wiped using Kim-wipes, and dried with a blow-dryer for 20 seconds to remove the free/excess water left on the fiber surface. After weighing, the fibers were placed again in the steam environment for subsequent tests.

SFM15PP85-190 fibers were dyed using a McCormick red food dye. The fibers were directly soaked into the liquid dye. After 10 min, the fibers were washed with DI water for 5 times. Neat PP fibers were used as a control.

3.3. Results and Discussion

3.3.1 Thermal Degradation

Thermal gravimetric analysis was performed to determine the thermal stability of the SFM/PP blend, which is essential for melt-mixing and subsequent melt-spinning. Figure 21 displays the results for 30/70 wt% SFM/PP blend for different isothermal runs with holding temperatures ranging from 160 to 250°C. As expected, the blend displays the most stable response at the lowest temperature of 160°C, and weight loss observed at 160°C for a holding time of 20 min is less than 0.1%. At higher temperatures, the blend has a weight loss of about 0.2 wt% at 190°C and 0.6 wt% at 220°C, for a holding time of 2 min. The weight loss increases to about 0.5 wt%, 1.8 wt%, and 5 wt% at 160, 190, and 220°C, respectively, for a longer holding time of 20 min.

At the highest temperature examined in this study, 250°C, the weight loss increases significantly from 2 wt% for 2 min holding time to about 10 wt% for 20 min holding time. The above results establish that SFM/PP has good thermal stability for processing at 160°C and 190°C, but only moderate stability at 220°C. At 250°C, there is a sharp increase in the thermal degradation level. In a previous chapter, we were shown that monoglyceride displays a drastic weight loss around 250°C (Guzdemir et al. ⁶⁸). Higher temperature and residence time accelerates the degradation of soy flour and also monoglyceride ⁶⁸ while PP stays stable at this temperature ⁵².

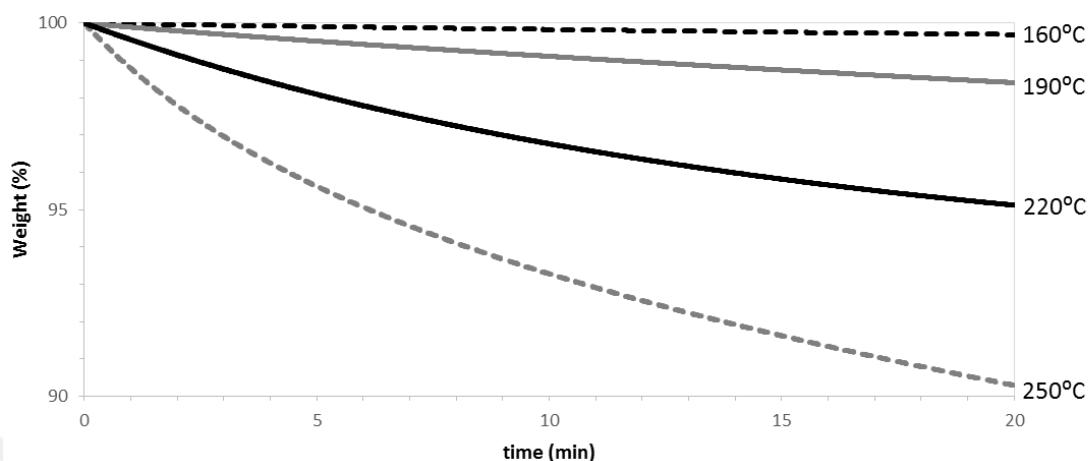


Figure 21. Isothermal thermogravimetric scans at 160⁰C, 190⁰C, 220⁰C and 250⁰C for blends having 30 wt% SFM and 70 wt% PP (SFM30PP70).

3.3.2 Effect of temperature on fiber spinnability and properties

Based on thermal stability analysis, fiber spinning temperatures were chosen as 160, 190, and 220⁰C. The mixing time and spinning time were determined as 2 min and 20 min, respectively. Limited fibers were also spun at 250⁰C to confirm the degradation observed in TGA results. For 15 wt% filler content, SFM15-PP85 fibers were successfully produced by melt-spinning, as displayed in Figure 22. The average fiber diameters were measured at 65±11, 59±4, 50±6, 107±27 μm at 160⁰C, 190⁰C, 220⁰C, and 250⁰C, respectively.

At the lowest temperature of 160⁰C, the SFM/PP blend was highly viscous, as expected. Consequently, the spinnability of the blends was limited. At 190⁰C and 220⁰C, the flow was smooth, and extensibility of the blend increased, so it resulted in finer fiber diameters. This observation is consistent with independent rheological measurements,

shown in Figure 22. The power-law parameters were shown in Table 8. The shear viscosity of the blend at 160⁰C is twice of that at 190⁰C, i.e., as expected viscosity decreased as temperature increased. This is consistent with prior literature results that confirm that at higher melt temperatures, polymer blends have higher extensibility and easier draw-down¹⁰⁴. At 250⁰C, soy flour degradation limited the extensibility of the blend, and the final product was filaments with large diameters. Fiber diameter is an important feature because other properties are related to it.

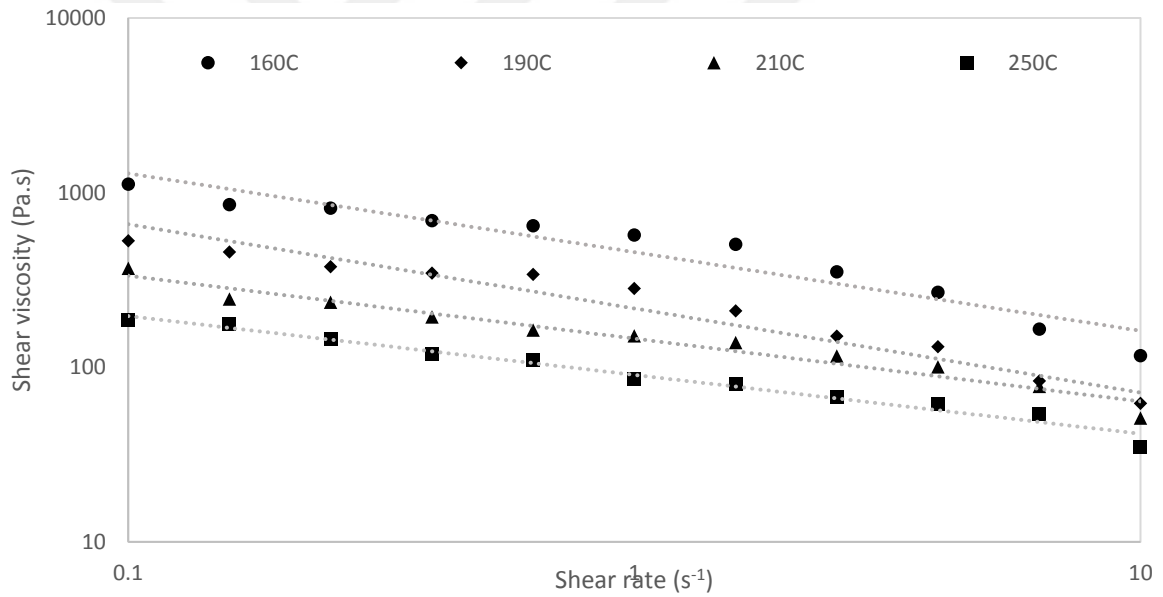


Figure 22. Shear viscosity of SFM15-PP85 blend at 160, 190, 220, and 250⁰C. Linear least square fit is shown by dotted lines for each sample.

Table 8. Power-law viscosity parameters, n and K , for soy/PP blends

Sample	N	K (Pa.s ^{n})
SFM15-PP85-160	0.55	457
SFM15-PP85-190	0.52	217
SFM15-PP85-220	0.64	146
SFM15-PP85-250	0.67	91

In addition, fiber color turned light brown at 160 and 190°C, as displayed in Figure 23. At 220 and 250°C, the fibers had a dark brown color because of significant soy flour decomposition. This result is in good agreement with the ones obtained by the thermal degradation test. The color change is likely due to Maillard reaction^{105,106} where the soy sugars and soy protein react leading to a decrease in the content of hydrophilic groups and improvement of some properties of soy flour like bonding strength¹⁰⁷. Darker shades were produced at increasing spinning temperatures due to increasing extents of the reaction^{106,108}.

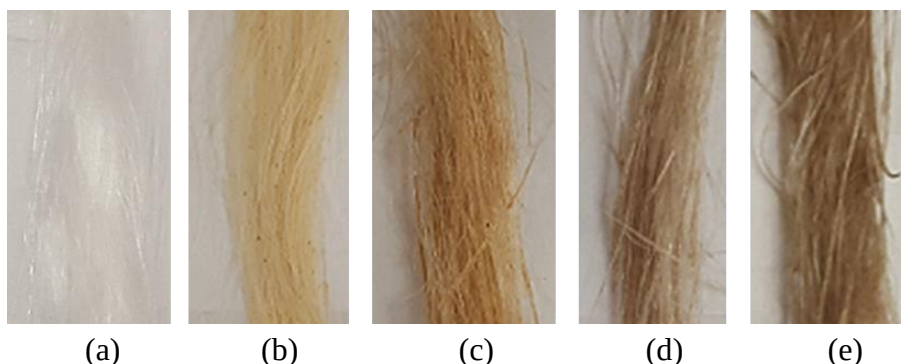


Figure 23. The representative color change image of (a) neat PP fibers and soy filled PP fibers (SFM15-PP85) spun at (b) 160°C, (c) 190°C, (d) 220°C and (e) 250°C

The tensile properties of the SFP15-PP85 fibers spun at four different temperatures are reported in Table 9, and stress-strain behaviors are shown in Figure 24. As the spinning temperature increased from 160 to 220°C, the yield stress decreased from 37±6 MPa to 19±4 MPa, which is an acceptable value for nonwoven fabrics. At 250°C, all fibers properties were reduced due to highly degraded soy flour. In comparison, neat PP displayed a tensile modulus, tensile strength and strain-to-failure values of 1224±136 MPa, 104±10 MPa, and 260±35%, respectively. Although lower than those of neat PP fibers, SFM/PP fibers processed at 160 and 190°C had similar tensile properties, but fiber spinning was easier at 190°C. Properties deteriorated significantly at 220 and 250°C. Therefore, for further studies, 190°C was chosen for subsequent mixing and spinning trials.

Table 9. Summary of mechanical properties of SFM15-PP85 soy flour-filled PP fibers

	Processing Temperature (°C)	Tensile Modulus (MPa)	Yield Stress (MPa)	Yield Strain (%)	Failure Strength (MPa)	Strain-to-Failure (%)
1	160	1313±419	37±6	4.8±0.4	95±30	275±42
2	190	914±164	29±3	5.0±1.0	74±7	268±57
3	220	743±217	19±4	3.8±0.7	63±9	276±41
4	250	207±108	4.5±2	2.6±0.9	11±5	106±48

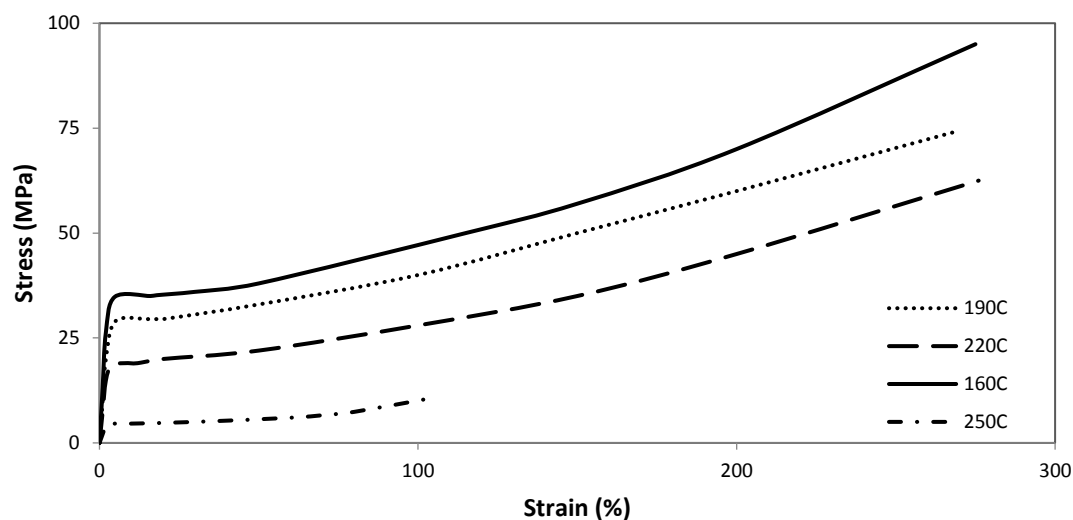


Figure 24. Stress-strain curves of SFM15PP85 fibers spun at 160, 190, 220, and 250°C.

SEM micrographs of the SFM/PP fibers are displayed in Figure 25 (a-j). All fibers have a nominally circular cross-section with some soy flour agglomerates evident in the lateral and cross-sectional micrographs. Generally, SFM/PP fibers have a rough surface as compared to the smooth surface of neat PP fibers.

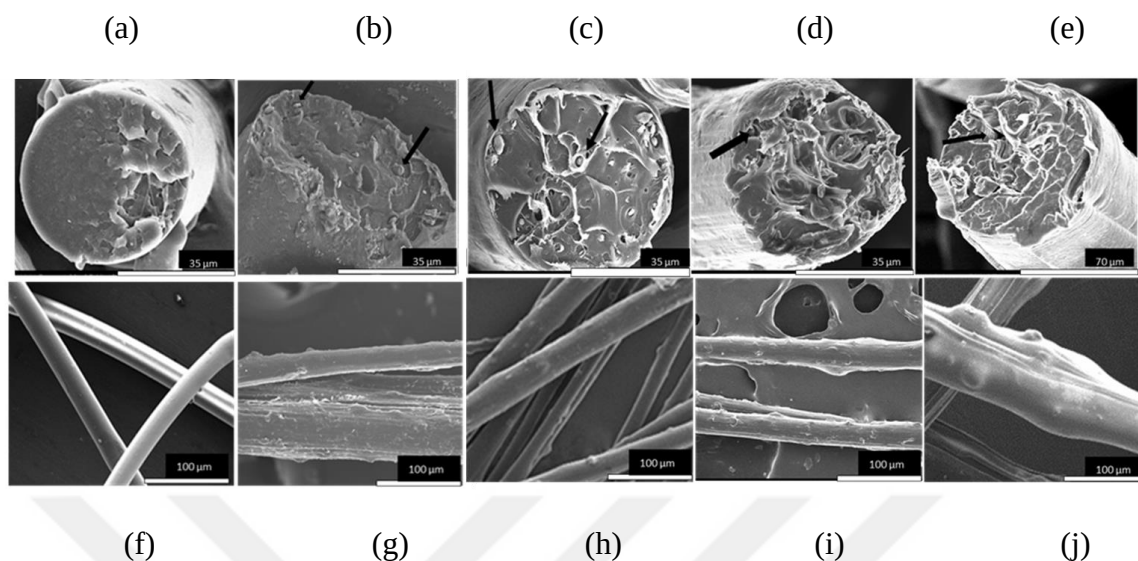


Figure 25. SEM micrographs of cross-sections of (a) neat PP, (b) SFM15PP85-160, (c) SFM15PP85-190, (d) SFM15PP85-220, and (e) SFM15PP85-250 fibers. Lateral area of the fibers are displayed in (f) neat PP, (g) SFM15PP85-160, (h) SFM15PP85-190, (i) SFM15PP85-220, and (j) SFM15PP85-250 fibers

3.3.3 Effect of Filler Composition on Mechanical Properties

Next, based on the results reported in the previous section, fibers filled with 5, 15, and 30 wt% SFM were spun at 190°C. Table 10 lists the mechanical properties of the fibers having different soy flour compositions. Also, stress-strain curves are displayed in Figure 26.

Table 10. Mechanical properties of the fibers spun at 190⁰C and containing 5, 15, and 30 wt% SFM. Also shown is the response of neat PP fibers

Fibers	Tensile Modulus (MPa)	Yield Strength (MPa)	Yield Strain (%)	Tensile Strength (MPa)	Strain-to Failure (%)
Neat PP	1224±136	37±3	5.0±1.3	104±10	260±35
SFM5PP95-190	843±140	32±4	5.5±0.5	97±16	294±46
SFM15PP85-190	914±164	27±3	5.0±1.0	74±7	268±57
SFM30PP70-190	674±245	18±4	6.1±2.6	44±11	275±42

The yield strain and strain-to-failure of SFM/PP fibers are not statistically different from those of neat PP fibers and are not affected by the soy composition, because the continuous phase, PP, dominates the strain behavior of the composite. Elongation of the fibers was not affected by soy flour inclusion at low soy contents.

The yield strength of soy/PP fibers decreased to 32 MPa, 27 MPa, and 18 MPa for 5, 15, and 30 % SFM/PP fibers, respectively, as compared with neat PP yield strength of 37 MPa. A similar decreasing trend was observed for tensile strength; values of 97, 74, and 44 MPa were measured for fibers containing 5, 15, and 30 % soy, respectively. The reduction of strength with increasing soy content is consistent with prior literature results of Sailaja et al.⁵⁴ for bulk soy/PP composites.

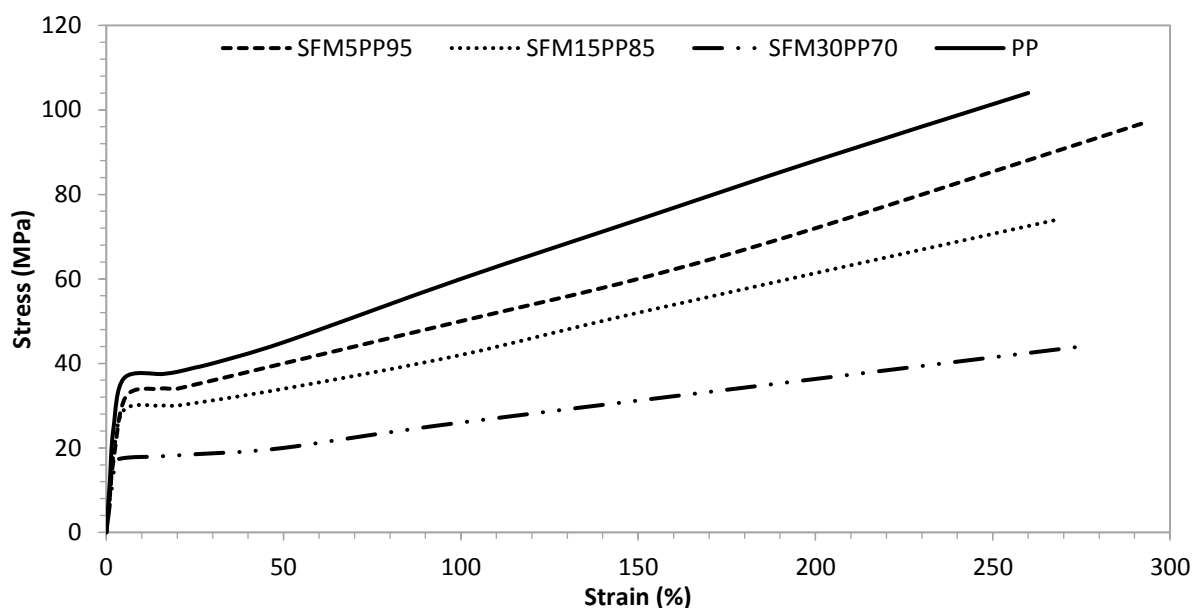


Figure 26. Stress-strain curves of SFM/PP fibers spun at 190°C with SFM contents of 5, 15, and 30 wt%

It is noted that while clays and hard inclusions lead to an increase in composite modulus¹⁰⁹⁻¹¹², inclusion of soy flour leads to a reduction in tensile modulus for 15 and 30 wt% composites, as compared to that of neat PP fibers. The decrease in tensile modulus is explained by the lower stiffness of soy flour. The reduced stiffness provides a softer feel to the composite fibers as compared to that of neat PP fibers. These results indicate that fibers containing up to 30 wt% soy flour have the potential to be used for disposable nonwoven fabrics.

3.3.4 Hydrophilicity /Coloring

For use in disposable nonwoven fabrics, other properties of fibers are also important and were investigated next. Some disposable nonwoven fabrics come in contact with water and body fluids, e.g., sanitary pads, diapers, and band-aids. Therefore, contact angles with water were measured for the three different soy contents of 5, 15, and 30 wt%. These measurements were performed on films obtained from pressing appropriate extrudates into films. The contact angles were measured at $101\pm 3^\circ$, $83\pm 3^\circ$, $53\pm 7^\circ$ and $34\pm 5^\circ$, respectively, for the blends having SFM contents of 0 (PP as control), 5, 15, and 30 wt%. Contact angles larger than 90° indicate a hydrophobic surface. The lower angles measured for SFM/PP surface revealed that presence of soy particles on the surface improved the hydrophilicity of the composite.

Figure 27 displays the moisture absorption characteristics of SFM/PP fibers at different compositions, with neat PP fibers included as a control. It is evident that neat PP fibers (i.e., without soy flour) have the lowest moisture absorption capacity with no measurable uptake (~ 0 wt%), consistent with the hydrophobic nature of PP. At 5 wt% soy content, the moisture gain by fibers was measured at 8 wt%. This is an indicator that soy flour on fiber surface improved hydrophilicity when added to the polymer.

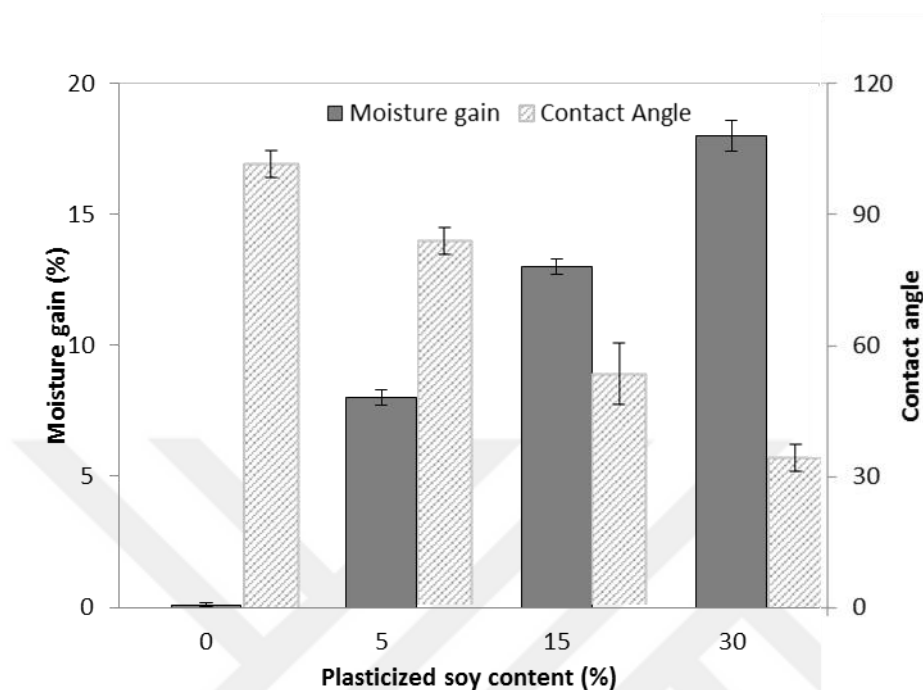


Figure 27. Moisture absorption of SFM/PP fibers and contact angles of SFM/PP blends having 5 wt% soy flour (SFM5PP95), 15 wt% SFM and 70 wt% PP (SFM15PP85), 30 wt% SFM, and 70 wt% PP (SFM30PP70). Also shown are data for PP (control) fibers (0 wt%). The absorption test was done for 1 hour.

At 15 wt% soy flour, the fiber weight gain was 13%, increasing to 18 wt% for composite fibers containing 30 wt% soy. This hydrophilic fiber property is desirable in many nonwoven fabrics that come into contact with human skin, such as in disposable/sanitary applications.

To determine the extent of deterioration of fiber properties, tensile testing was also conducted on fibers exposed to moisture. Also, as displayed in Table 11, the fibers

preserved almost 90% of their tensile properties. Therefore, the fibers are suitable for applications where the fabrics may be exposed to moisture.

Table 11. Mechanical properties of SFM15PP85-190 fibers before and after moisture-contact. Pure PP fibers were used as control samples.

Fibers	Tensile Modulus (MPa)	Yield Stress (MPa)	Yield Strain (%)	Tensile Strength (MPa)	Strain-to-Failure (%)
Before moisture-contact					
PP	1210±122	36±3	5.1±1.1	100±12	262±31
SFM15PP85-190	914±164	27±3	5.0±1.0	74±7	268±57
After moisture contact					
PP	1214±83	43±6	7.4±1.0	90±25	215±47
SFM15PP85-190	780±96	28±5	5.4±1.2	58±9	247±61

Another desired property for any textile product is its colorability. Figure 28 displays neat and filled PP fibers before and after coloring in a red food dye. While control sample (neat PP fibers) could not absorb any color after immersion in colored water for 10 min, SFM/PP fibers turned light pink on the matrix; the red dots on the fiber represent soy agglomerates. This observation is consistent with the studies showing that neat PP is hard

to dye with organic colors by classical methods because of its non-polar (purely aliphatic) structure as well as high crystallinity ^{113,114}. Increased hydrophilicity provides ease of coloring to the fibers. In addition, even without any coloring, SFM/PP fibers have a tan color that resembles some natural fibers like flax that have potential for disposable nonwovens.

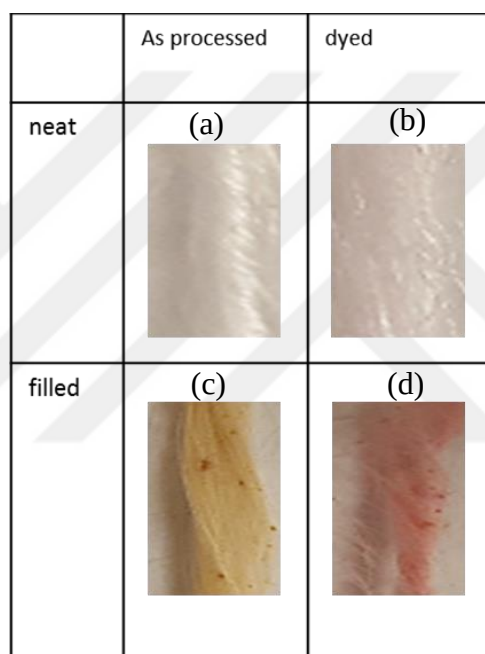


Figure 28. Images of (a) PP fibers before immersion, (b) PP fibers after immersion in a red food coloring, (c) as-spun SFM/PP fibers (SFM15PP85-190) before immersion, and (d) dyed SFM15PP85-190 fibers

Nonwoven forming ability

Finally, to assess the potential of these biocomposite fibers for conversion into nonwoven fabrics, a limited quantity of soy-PP fibers were thermally compacted in a hydraulic Carver press using textured metallic plates. As shown in Figure 29, a single fiber

was bonded to other single filaments and so a prototype non-woven fabric sample was successfully obtained. This confirms the retention of thermoplastic characteristics of the composite fibers necessary for subsequent nonwoven fabric production.

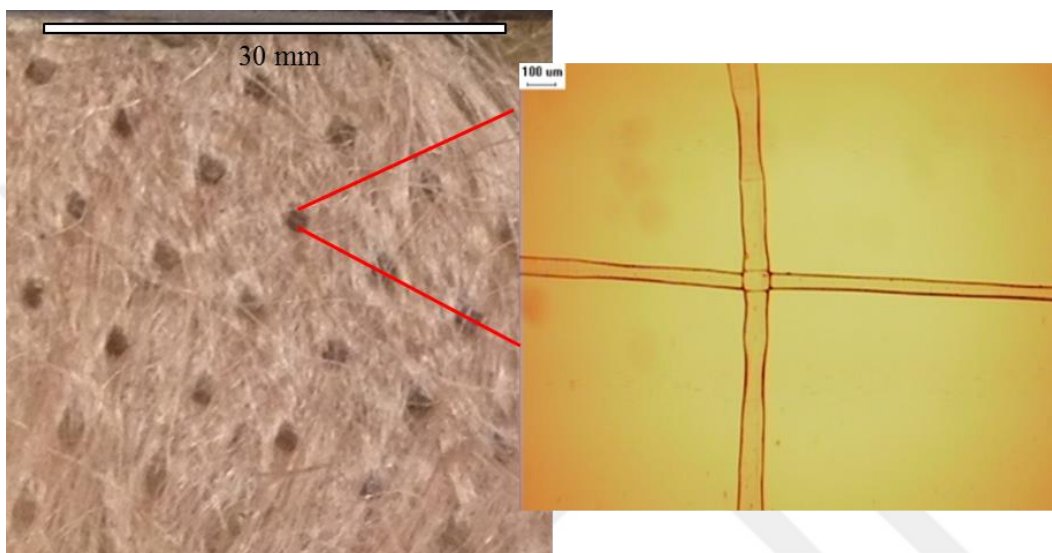


Figure 29. An image of SFM15-PP85-190 nonwoven with an inset displaying a representative optical micrograph of a bonding point between two single-filaments. The fibers were hot-pressed at 125⁰C for 1 min.

3.4. Conclusions

Soy flour (SF) was successfully incorporated into PP fibers using a scalable melt-spinning route. SFM/PP fibers, having 15 wt% soy, spun at 190⁰C showed 25% less tensile modulus and tensile strength than those of neat PP fibers. As the spinning temperature increases from 160⁰C to 220⁰C, yield stress decreased monotonically with processing temperature from 37±6 MPa to 19±4 MPa due to the increased thermal degradation of soy flour. Tensile modulus and strengths were adversely influenced by increasing soy content,

but the strain-to-failure was not significantly affected. The inclusion of SFM by 15 wt% resulted in fibers with a tensile modulus of 914 ± 164 MPa and a tensile strength of 74 ± 7 MPa, compared to neat PP fibers with a tensile modulus of 1224 ± 136 MPa and a tensile strength of 104 ± 10 MPa. Based on experiments conducted at different processing temperatures and different soy contents compositions, a spinning temperature of 190°C and a soy content of 15 wt% provided ease of processability combined with adequate retention of tensile properties of SFM/PP fibers.

Increasing soy flour content led to the fibers with improved hydrophilic characteristics. Moisture absorption studies revealed that the composite fibers containing 30 wt% soy gained 18 wt% moisture. Also, the presence of soy agglomerates on the surface provided the composite fibers a natural-fiber tactile feel and ease of colorability.

CHAPTER 4

MELT-SPUN POLY-(LACTIC ACID) FIBERS MODIFIED WITH SOY FILLER

4.1 Introduction

In Chapters 2 and 3, it was established that soy flour filled polyolefin blends are spinnable into fibers. Although these novel fibers are partially sustainable, the polyolefin phase of the fibers is non-biodegradable. Therefore, this chapter discusses the investigation of a biodegradable polymer, PLA, as the base polymer.

As discussed in Chapter 1, PLA has attracted interest due to its biodegradability, ease of processability, and good mechanical properties. However, PLA has a slow biodegradation rate and is significantly more expensive compared to its non-degradable petroleum-based counterparts. One way to reduce the cost and improve the biodegradation rate is to blend PLA with inexpensive bio-fillers like soy¹¹⁵. Several research studies have reported on the use of agricultural residues like starch, cellulose, and soy protein by incorporating them into PLA to form bio-composites^{58,59,116-120}. However, as discussed in Chapter 1, melt-spinnability/processing of soy/PLA fibers has not been systematically investigated in prior literature studies. Therefore, the current chapter focused on the melt-spinning of PLA fibers modified with soy filler. The specific objectives were to (i) investigate the spinnability of soy-modified PLA, (ii) characterize fibers for their morphology and mechanical properties, and (iii) assess the effect of soy filler on fiber degradation.

4.2 Experimental

4.2.1 Materials

A fiber grade poly-(lactic acid), Ingeo Biopolymer PLA 6202D (Nature Works LLC), was used throughout this chapter. PLA 6202D has a density of 1.24 g/cc and a melt flow index of 15-30 g/10min. Soy flour (ADM, Decatur, IL) that was used earlier for PE and PP-based fibers was also used to incorporate into PLA. It contained nominally 53% protein, 30% carbohydrate, 7% moisture, 1 % fat, and remainder dietary fiber. All materials were dried at 80°C for 4 hours in a vacuum oven before processing.

4.2.2 Melt-spinning

Fibers were prepared by a two-step process involving melt-compounding followed by melt-spinning as described in previous chapters 2 and 3. Polyolefins used in Chapters 2-3 have larger molecular weight and excellent spinnability. Also, the resulting polyolefin fibers are very ductile. In contrast, PLA is not as easily spun and the resulting fibers are an order of magnitude less ductile than polyolefin fibers. For this reason, soy filler content in PLA based fibers was limited to 5 wt%. The initial step was the melt-compounding of soy filler with PLA pellets using a 15 mL co-rotating twin-screw micro-extruder, DSM Xplore (Geleen, Netherlands). The equipment was operated in recirculation mode with a 2 min residence time. Compounding was done in the speed-controlled-mode with a rotation speed of 100 rpm. Two barrel temperatures, 200°C and 230°C, were used for two different experiments.

The second step, melt-spinning, was performed at the end of compounding run using the force-controlled-mode of the extruder. This provided a more even throughput during spinning. Fibers were continuously spun through a custom-designed, three-hole spinneret containing 500 μm diameter capillaries. The fibers were drawn-down using a take-up roll, and the process could be sustained over 30 minutes. To obtain experimental/prototype samples of nonwoven fabrics, SF-PLA fibers were compacted in a hydraulic Carver press at 1350 kg and 125 °C for 1 minute using textured metallic plates. Both fibers and nonwovens were stored in ziplock bags prior to testing.

4.2.3 Characterization

Tensile tests were conducted following the ASTM D2256 procedure on single fibers, with an initial gage length of 2.54 cm. Tests were performed at a cross-head speed of 0.25 cm/min with a 22 N load cell (Applied Test Systems Inc., Series 900). At least 5 replicates were tested from each group.

Thermogravimetric analysis (TGA) was performed on a Pyris1 instrument (Perkin Elmer Inc., USA). The samples were heated in an aluminum pan under a nitrogen atmosphere from 25°C to 500°C at a heating rate of 10°C/min.

Scanning electron microscopy (SEM, Hitachi S-4800, Hitachi, Japan) was used to assess the morphology of fibers by examining the cross-section and lateral surfaces. The fibers were cryogenically fractured for better cross-section images and sputter-coated with platinum to avoid charging. Optical microscopy (BX60; Olympus Corp., Lake Success, NY) was used to measure single fiber diameters and investigate the non-wovens.

Hydrolytic degradation studies were performed on fibers about 5 cm long. Approximately 20 mg from each sample was put into separate vials filled with 0.1 M and 1 M NaOH aqueous solutions. The vials were maintained at two different temperatures, 25°C and 37°C. The fibers were removed from the vials and placed in a vacuum oven for 12 hours at 80°C to dry, and the mass loss of fibers was recorded. Three replicates were used for each sample. The samples were immersed in various solutions for up to three days.

4.3 Results and Discussions

4.3.1 Fiber Melt-Spinning

Thermal stability of soy filler is one of the main challenges faced during processing because melt-mixing it into PLA necessitates temperatures in excess of 200°C (about 20-30°C above PLA melting point) ¹²¹. To obtain thermal degradation characteristics of the SF-PLA, TGA was conducted and thermograms are displayed in Figure 30. The inclusion of soy flour into PLA resulted in a decrease in the measured onset decomposition temperature from 345°C to 322°C. At 500°C, the retained weight was measured at 4% for the SF-PLA blend.

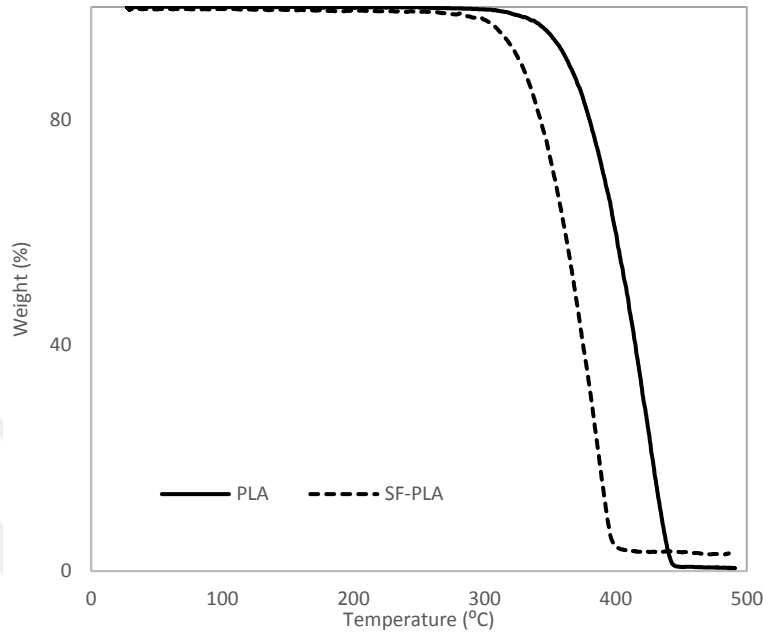


Figure 30. Comparison of thermal degradation neat PLA and SF-PLA under nitrogen atmosphere

Differential scanning calorimetry (Q1000 TA Universal Inst, USA) for soy-PLA fibers was conducted to obtain glass transition, melting, crystallization, and cold crystallization temperatures. Aluminum pans were used for each sample with an average sample mass of 5 mg. The heating and cooling scan rates were 10⁰C/min under a nitrogen atmosphere from 25⁰C to 190⁰C. The degree of crystallinity was calculated from measured heats of fusion (ΔH_f), cold crystallization (ΔH_{cc}), and estimated ΔH_f^0 (93 J/g), using the following equation¹²⁵:

$$w_c = (\Delta H_f - \Delta H_{cc}) * 100 / (\Delta H_f^0 * 0.95).$$

Table 12 presents a summary of results for PLA and PLA-SP fibers. All fibers showed cold crystallization, glass and melt transitions as shown in Figure 31. The glass transition temperature of PLA was observed at 60⁰C. The addition of soy protein in the PLA matrix caused a slight decrease (~3-8⁰C) in T_g. Similarly, the melting transition of the composite fibers was affected by SP fillers and showed lower melting temperatures. The calculated crystallinity of neat PLA fiber was slightly lower than those of PLA-SP fibers. This observation indicates that soy protein slightly enhanced the extent of crystallization and possibly contributed to the lower ductility of the biocomposite fibers. Also, an exothermic peak was observed for all fibers that can be attributed to cold crystallization. Neat PLA has a slightly higher temperature (107⁰C) of cold crystallization as compared to that of biocomposite PLA-SP fibers. Further, PLA-SP fibers showed slightly higher crystallinity. Previous studies have shown similar results indicating that soy fillers enhance the crystallinity of PLA by acting as heterogeneous nucleating agent ^{57,59,126}

Table 12. DSC results of neat PLA and PLA-based composite fibers

Sample	T _{m1} (⁰ C)	T _{m2} (⁰ C)	ΔH _m (J/g)	T _g (⁰ C)	X _c (%)	T _{cc}	ΔH _{cc} (J/g)
PLA	155	162	31	60	29	107	27
PLA-SF	147	155	34	52	34	100	30

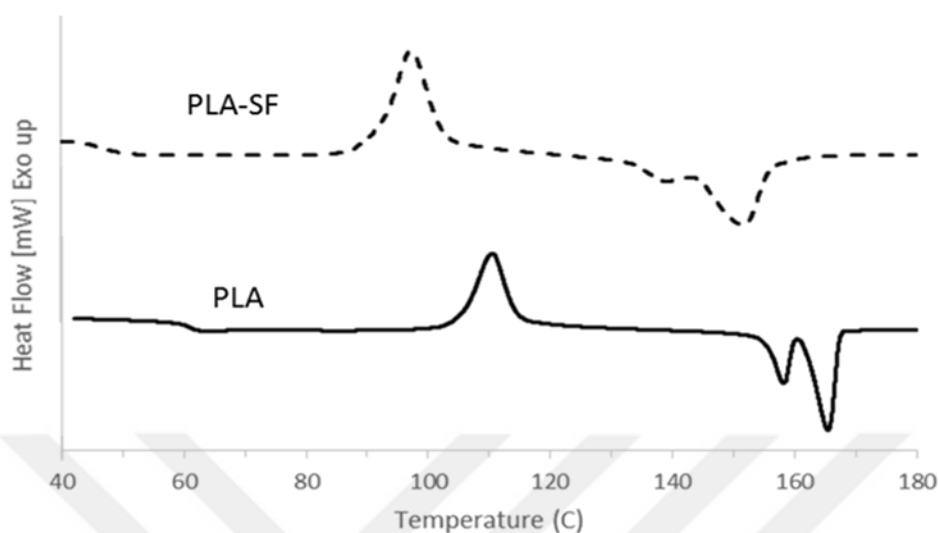


Figure 31. DSC thermograms of neat PLA fiber and PLA-based composite fibers

Based on the TGA results, melt compounding temperatures were held below the first peak degradation temperature. The viscosity of PLA and SF-PLA blend as a function of shear rate is displayed in Figure 32. Soy flour inclusion in PLA resulted in a higher viscosity at the lowest shear rates, $0.1\text{--}1\text{ s}^{-1}$, at both 200°C and 230°C . SF-PLA showed a shear thinning behavior with a power-law index of 0.50 while PLA behaved like a Newtonian fluid with a power-law index of 0.94. As expected, increased temperature resulted in a lower viscosity, so the extrusion was smoother at the higher temperature of 230°C .

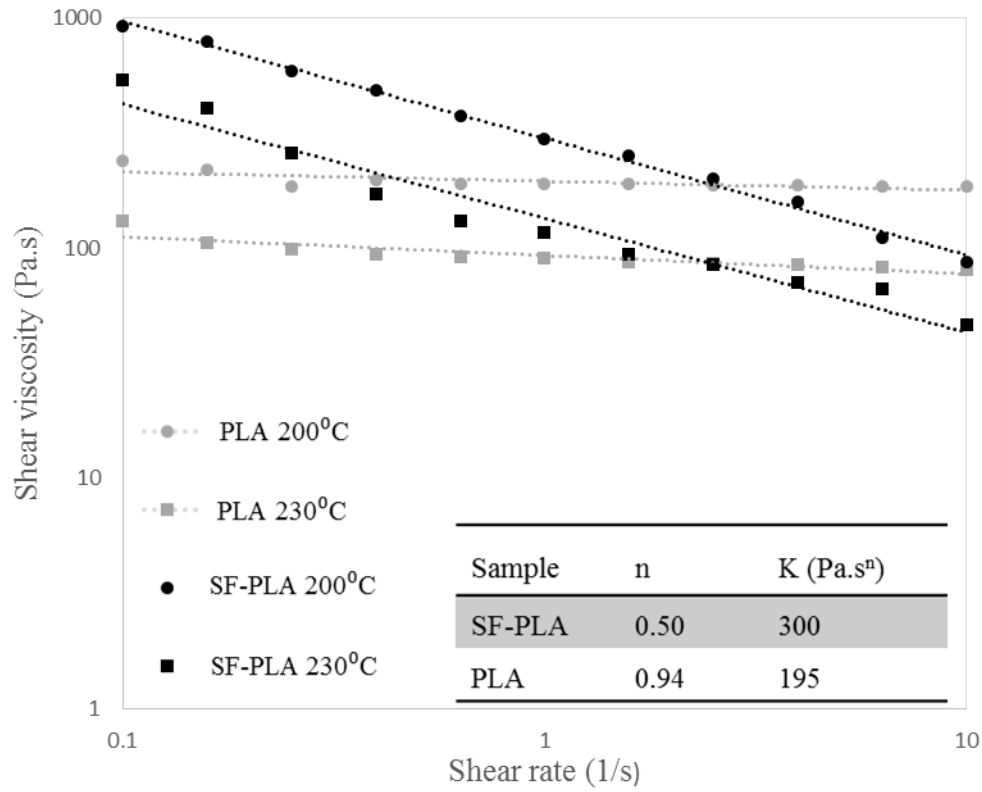


Figure 32. Shear viscosity of PLA and SF-PLA blend at 200 and 230°C. The dotted lines represent power-law fit. Inset table displays power-law viscosity parameters of PLA and SF-PLA: $\eta = K (\dot{\gamma}^{n-1})$ where η (Pa.s) is viscosity, K is consistency index (Pa.sⁿ), n is flow behavior index and $\dot{\gamma}$ is shear rate (s⁻¹)

Two different processing temperatures were used to spin fibers: 200 and 230°C. PLA fibers with and without soy filler were successfully spun. PLA melt spinning involved a draw-ratio of about 130, where the draw-down ratio (DDR) is defined as the square of the ratio of spinneret diameter to the final fiber diameter, $(D_o/D_f)^2$. The attainable DDR was sensitive to the addition of soy filler and found to decrease significantly at 5 wt% soy

content. So, higher soy contents were not incorporated in this study. This is consistent with prior results by Pötschke et al.¹²² where the draw-down characteristics of PLA fibers decreased with increasing filler concentration. PLA-based nanoclay composite fibers with a filler content of 4 wt% have been reported to be spun with a maximum draw-ratio of only 3.5¹²³.

4.3.2 Fiber Morphology and Size

The lateral surface of the fibers (i.e., along the length), as characterized by scanning electron microscopy, are shown in Figure 33(a-b). SF-PLA fibers have non-uniform diameters while neat PLA fiber diameters are uniform. PLA fibers had an average diameter of $44 \pm 7 \mu\text{m}$. For soy-modified fibers spun at 200°C , the diameters were measured at $52 \pm 13 \mu\text{m}$. The slight diameter increase of soy-modified fibers spun at 200°C can be attributed to the decrease of melt-stretchability. The diameters of the composite fibers spun at 230°C were found to range between 23 and $48 \mu\text{m}$. The higher spinning temperature resulted in improved drawability, which resulted in slightly thinner fibers.

The micrographs reveal that neat PLA fibers have a smooth lateral surface, but the soy-modified fibers have a rougher surface resulting from a few filler aggregates persisting through the melt-mixing step. This is partly expected due to the thermodynamic immiscibility of soy and PLA. Also, in this study, PLA and soy were only mechanically compounded. The roughness is an advantage for textile fibers because it improves the tactile properties of the fibers by reducing the ‘plastic-like’ synthetic feel. Also shown in Figure 33(c-d) are the fiber cross-sections. Neat PLA fibers exhibit a smooth surface with

some striations that might have formed during the cryo-fracturing process. In contrast, soy-filled fibers have rougher textures with some holes (identified with arrows) where the soy agglomerates have been pulled out during sample preparation.

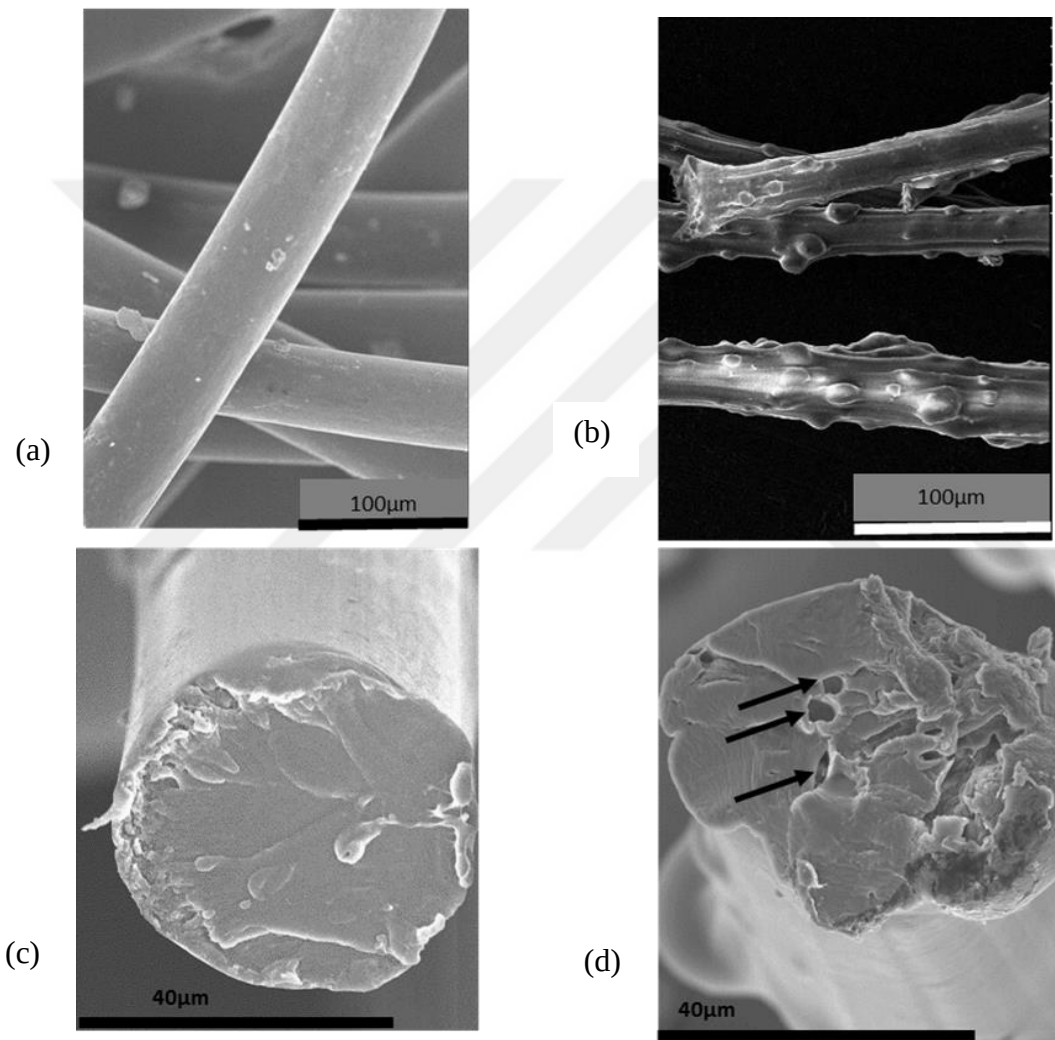


Figure 33. SEM micrographs of the lateral area of (a) neat PLA and (b) SF-PLA fibers at 200°C. Cross-sections are displayed in (c) neat PLA and (d) SF-PLA fibers (Black arrows indicate the roughness of the fiber cross-section due to the soy filler.)

4.3.3 Tensile Properties

Representative stress-strain curves of SF-PLA and neat PLA fibers are presented in Figure 34. Values for the tensile modulus, strength, and strain-to-failure are summarized in Figure 35(a-c). The fibers spun at 200⁰C showed tensile modulus of 2.7±0.2 and 2.5±0.3 GPa for neat PLA and SF-PLA fibers, respectively. The higher processing temperature of 230⁰C resulted in a decrease in tensile modulus to 1±0.4 GPa for SF-PLA fibers, respectively. Lower modulus reflects low rigidity characteristic of soy filler, which provides less stiffness.

For the fibers spun at both spinning temperatures (200 and 230⁰C), a decrease was observed in the tensile strength of SF-PLA fibers as compared to that of neat PLA fibers. The fibers spun at 200⁰C showed tensile strength of 74±2 and 44±5 MPa for neat PLA and SF-PLA fibers, respectively. A similar trend has also been observed for other polymeric fibers filled with soy flour (Guzdemir et al.⁶⁸). The lower strength of SF-PLA composite fibers compared to that of neat PLA fibers can be explained by the lack of filler-matrix adhesion due to the polar soy and nonpolar PLA, which results in poor stress transfer. The high processing temperature of 230⁰C resulted in a decrease in tensile strength to 39±13 for SF-PLA fibers

With the addition of soy flour, as shown in Figure 35(c) strain-to-failure decreased from 48±5% to 8±3% that were spun at 200⁰C. As shown on the stress-strain curves (Figure 34), SF-PLA fibers did not show any obvious yielding before failure. Also, as expected, the fibers spun at 230⁰C were found to have less ductility than that of the fibers

spun at 200°C. The low ductility of SF-PLA fibers can be attributed to the fact that PLA has much lower ductility as compared with PE and PP. Therefore, it can be filled with a significantly less filler content, i.e., 5 wt% only. Thus, future work should address the incorporation of larger filler contents and the needed compatibilizers.

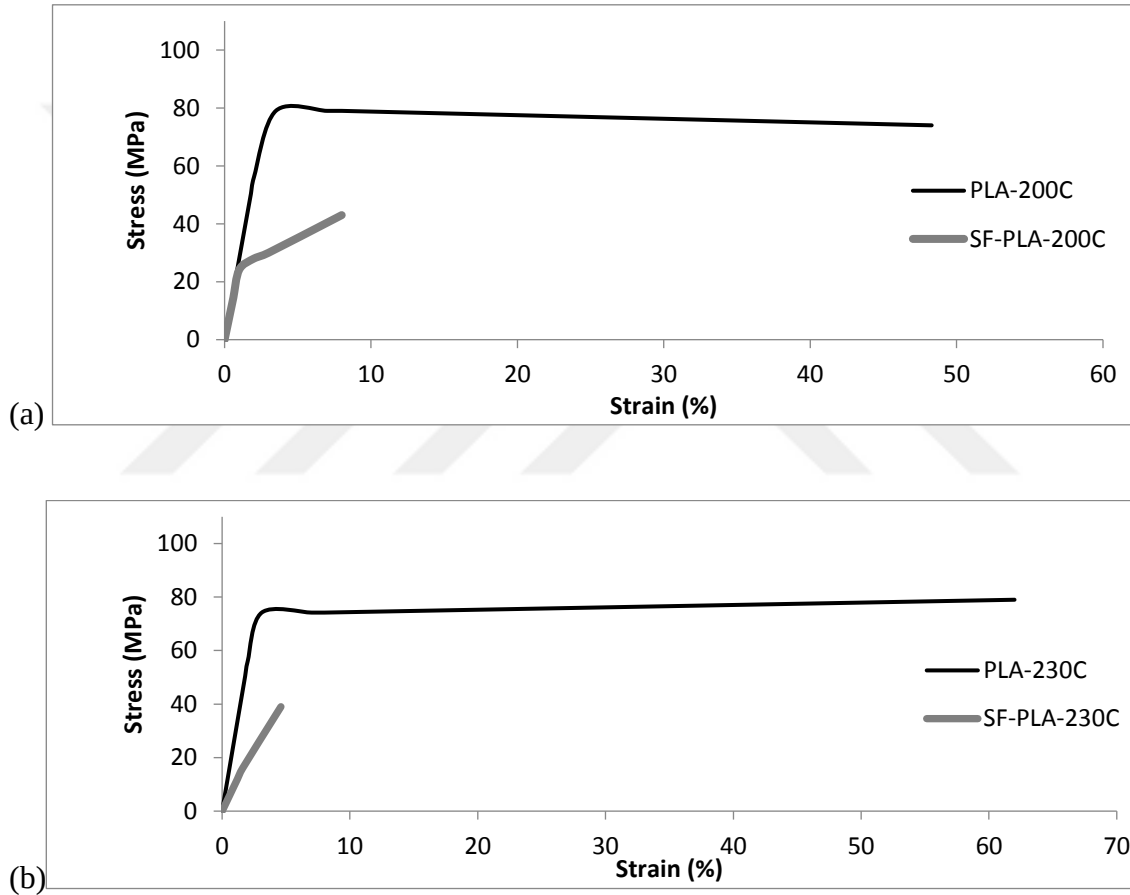


Figure 34. Stress-strain curves of SF-PLA fibers spun at (a) 200°C and (b) 230°C

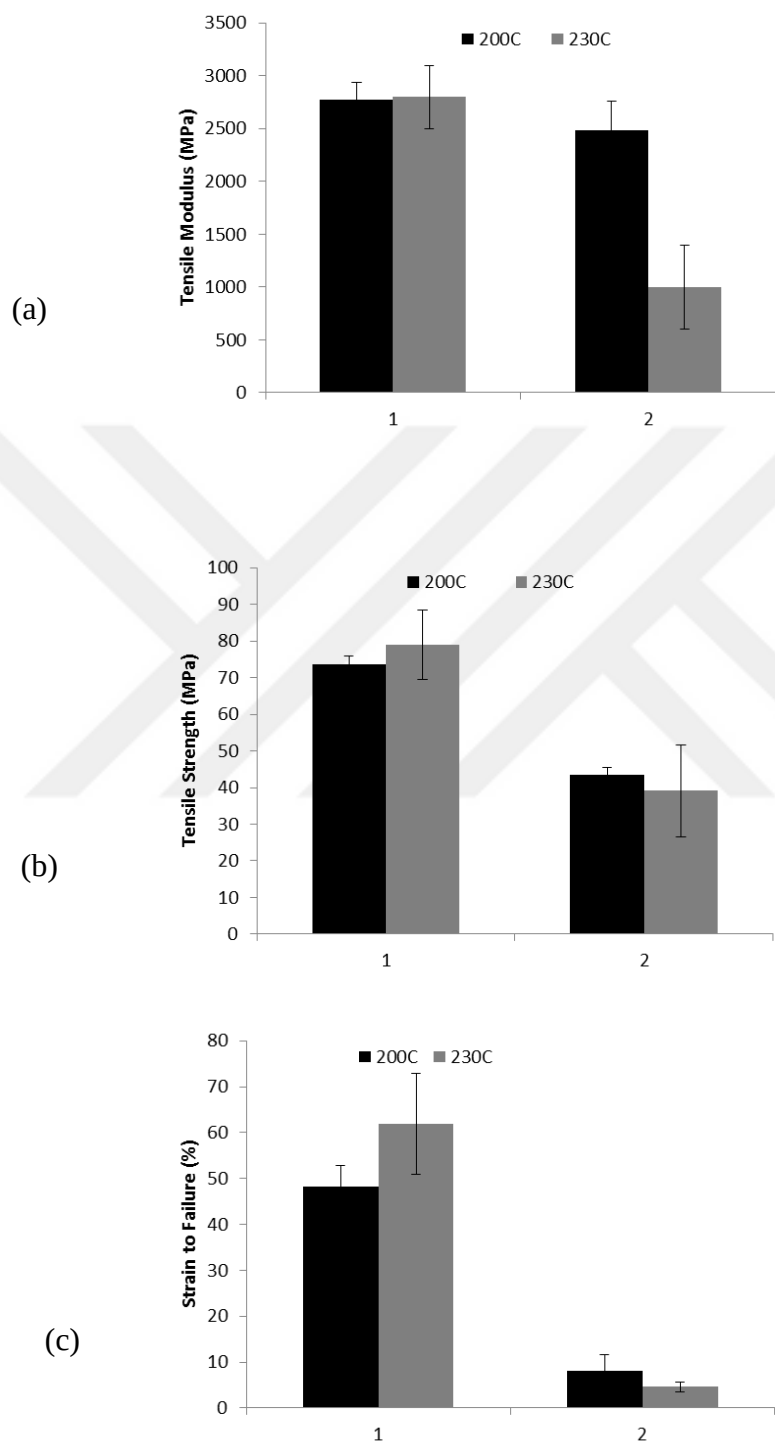


Figure 35. (a) Tensile modulus, (b) tensile strength, and (c) strain-to-failure of neat PLA (1) and SF-PLA (2) fibers spun at 200°C and 230°C

4.3.4 Hydrolytic Degradation

Based on the above results that showed better tensile properties for fiber spun at the lower temperature that minimized soy degradation, the remaining experiments were conducted on fibers spun at 200°C. To determine the effect of soy filler on hydrolytic degradation of PLA fibers, an accelerated degradation study was conducted on the fibers exposed to 25°C and 37°C in 0.1 M and 1 M aqueous NaOH solutions for 3 days. Figure 36 represents the visual observation of the fibers before and during the degradation.

The mass retention of various fibers at 0.1/ 1 M, and 25/ 37°C as a function of time during the degradation are displayed in Figure 37. Neat PLA fibers degraded entirely in approximately 75 hours in 0.1 M (pH=13) and in 50 hours in 1 M (pH=14) aqueous NaOH solutions. As expected, the mass reduction of fibers was higher in higher pH media. At the end of the first day of the experiments, the weight of the fibers decreased to 24.8% and 13.7% for SF-PLA fibers at 25°C, in 0.1M and 1 M, respectively. Higher pH medium resulted in faster degradation. This result is consistent with the results presented by Xu et al.¹²⁴ who reported that complete PLA degradation occurred in 3 days in a stronger alkaline solution, about five times faster than that in water. In the current study, all composite fibers disappeared in about 50 hours, as shown in Figure 36. As expected, the degradation rate of neat and composite fibers increased at 37°C, consistent with studies reported in the literature¹²⁵.

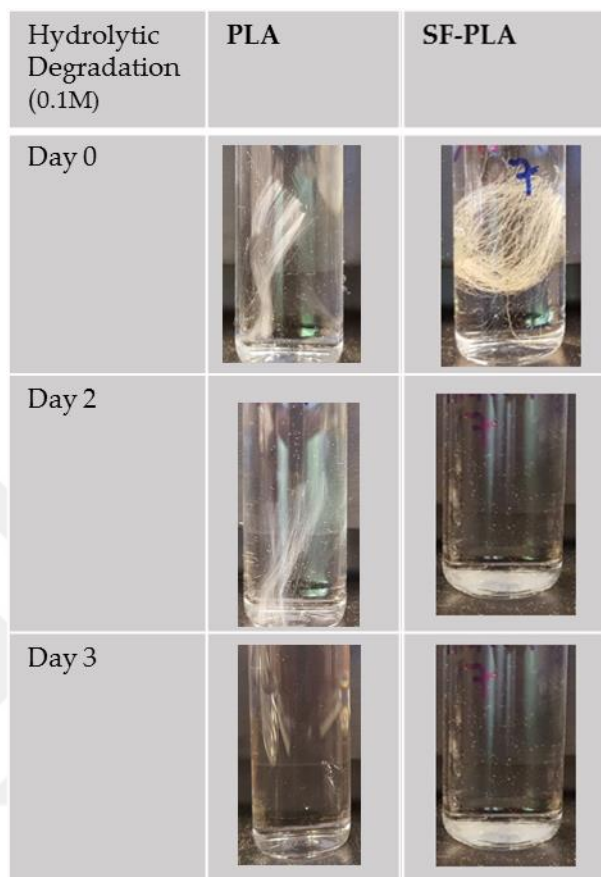


Figure 36. Images taken of PLA and SF-PLA fibers exposed to 0.1M aqueous solution at 25°C at day 0, 2 and day 3

Hydrolysis of PLA was approximated using first-order irreversible kinetics, and the rate constants for various fibers were obtained. Then, the remaining mass during degradation scales as e^{-kt} with respect to the initial mass (M_0) and degradation time (t).

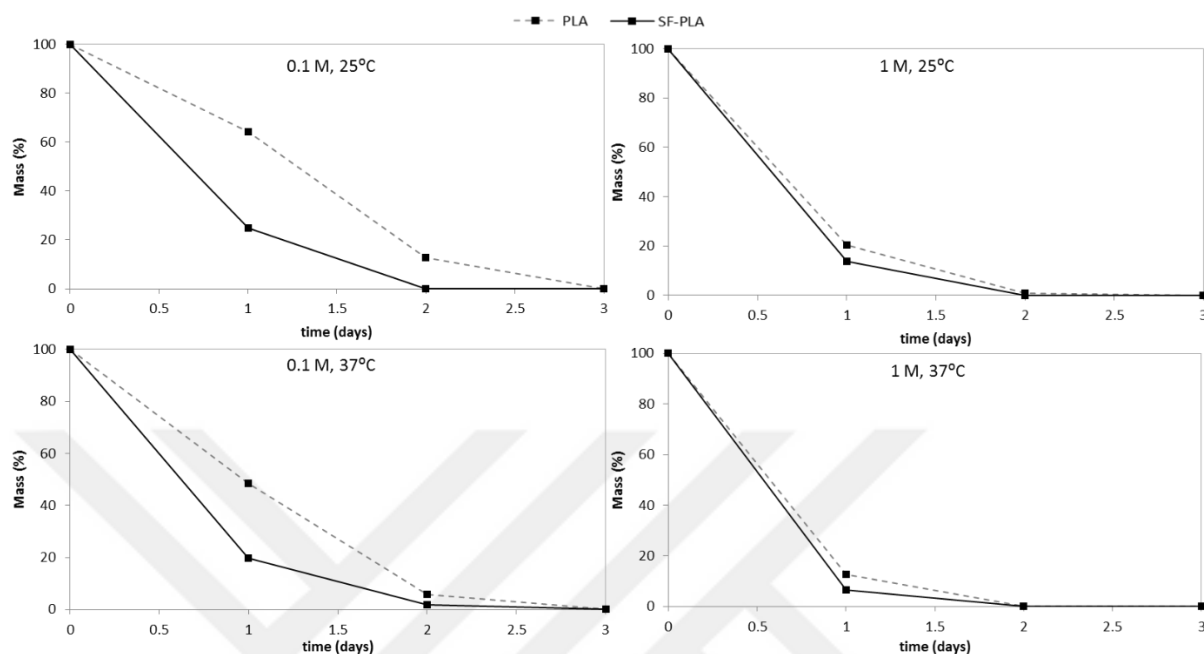


Figure 37. Mass retained of PLA and SF-PLA fibers during 3-day-hydrolytic degradation in 0.1 and 1 M NaOH aq. solution at 25°C and 37°C.

The pseudo-first-order rate constant, k , for composite fibers containing soy was about 4 to 5 times larger than that of neat PLA fiber indicating the overall acceleration of hydrolytic degradation of the fibers due to the presence of soy filler. It is noted that the overall degradation rate is a function of the rate constant and the surface area available for the hydrolytic attack¹²⁴. The composite fibers had extended internal surface area, as shown earlier in Figure 33, which led to increased reaction area and faster overall degradation.

Finally, to assess the potential of soy-PLA fibers for conversion into nonwoven fabrics, a limited quantity of SF-PLA fibers were thermally compacted in a hydraulic Carver press using textured metallic plates. As shown in Figure 38, a prototype non-woven

fabric sample was successfully obtained. Because surface fusion was still possible, SF-PLA fibers could be converted into the non-woven fabric. This confirms the retention of thermoplastic characteristics of the composite fibers necessary for subsequent nonwoven fabric production.

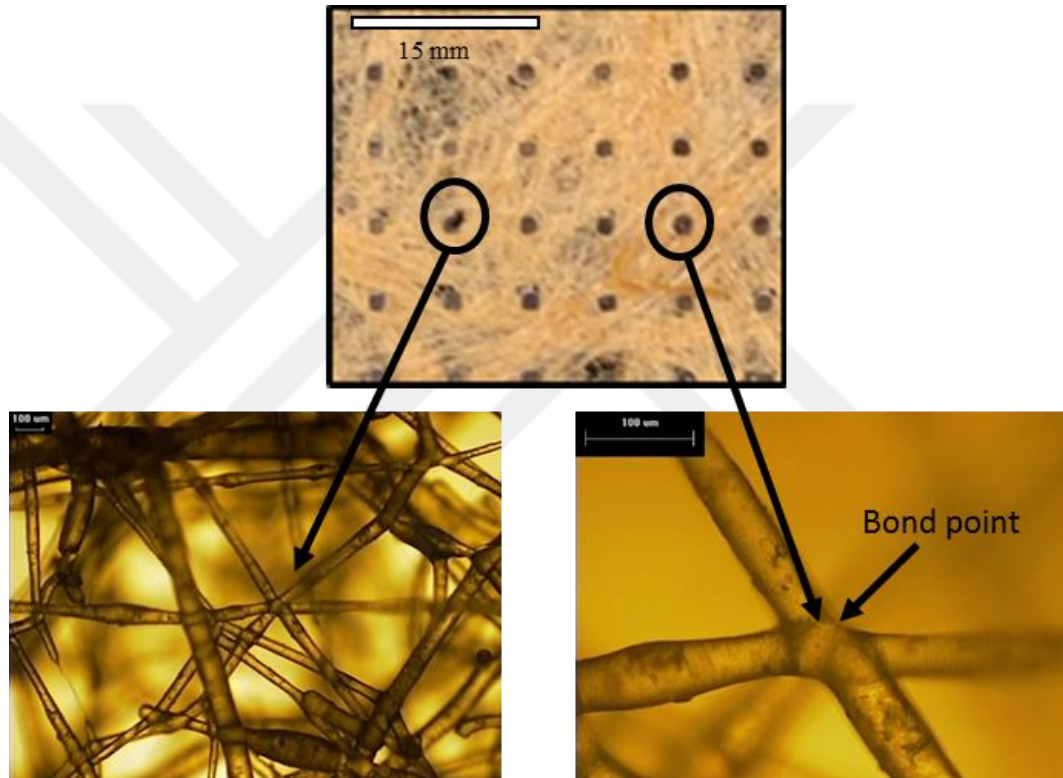


Figure 38. Image of SF-PLA non-woven and its optical micrographs

4.4 Conclusions

Fibers were successfully melt-spun from blends of soy particulates incorporated in a PLA matrix. After melt compounding of PLA and soy filler, the melt drawability decreased some, but was enough to obtain fibers as thin as about 25 µm using a nominal

draw-ratio of 100. The soy-PLA fibers were found to have a rough surface due to the presence of soy agglomerates, which is desirable because roughness improves the tactile properties of the fibers by reducing synthetic plastic-like feel. The tensile strength and modulus of soy-PLA fibers were lower than that of neat PLA. However, the overall values of ~39 MPa and 1 GPa for tensile strength and modulus indicate the significant potential of such fibers for disposable nonwoven fabrics. More importantly, the presence of degradable soy filler contributed to the overall acceleration of hydrolytic degradation of PLA composite fibers by providing increased surface area. Thus, the results from this chapter have established the feasibility of melt-spinning of soy-PLA fibers for potential use in bio-based nonwoven fabric applications requiring fast degradation.

CHAPTER 5

CONCLUSIONS AND FUTURE WORK

5.1 Conclusions

The overall goal of this research was to utilize soy products as fillers in polymeric matrices via the continuous melt-spinning route in order to reduce the dependency on synthetic polymers for the disposable textile applications. The goal was successfully accomplished, and the specific findings are summarized below.

In Chapter 2, it was established that soy filled polyethylene blends were spinnable using monoglyceride as a compatibilizer at 7 wt% content with 23 wt% soy. The processability and properties of soy-PE were optimized with regards to the soy and monoglyceride content. The blend with 23 wt % soy, 7 wt % M, and 70 wt % PE composition showed similar rheological behavior to that of pure PE. Without a compatibilizer, soy could not be adequately dispersed in PE, and the spinning was unsuccessful due to the high viscosity and phase separation at high soy content. At lower soy content, the spinning of Soy-PE fibers was successful without a compatibilizer. Small soy agglomerates on fiber surface provided the fibers with a tactile feel more similar to that of natural fibers, and less plastic-like. However, they had weak mechanical properties. Soy-M-PE fibers had a tensile modulus about 35% less than that of pure PE fibers. Lower modulus imparts softness to the fibers, which is desirable for textile use. Soy-M-PE fibers had yield and tensile strengths of 15 ± 1 and 57 ± 8 MPa, respectively, than pure PE fibers, that are adequate for potential use in disposable non-wovens. The analysis of the fibers,

using Fourier transform infrared (FTIR) spectroscopy, indicated that there was only mechanical interaction between soy-monoglyceride and PE-monoglyceride. Soy-M-PE fibers had low contact angle and improved moisture absorbability, so hydrophilic properties. The hydrophilic behavior, coupled with a desired tactile feel provided by the textured surface, indicates the potential use of the soy-PE fibers in disposable nonwovens.

In Chapter 3, soy flour was successfully incorporated into PP fibers using a scalable melt-spinning route. The most widely used polymer in disposable nonwovens, PP, was investigated as the matrix of the soy flour filled composite fibers. Although PP is a polyolefin similar to PE (a higher homolog), it has a melting point 30°C higher than that of PE. Therefore, the thermal stability of soy-filled PP was established at higher temperatures. The effect of processing temperatures from 160°C to 250°C was investigated on the spinnability and fiber properties. As the spinning temperature increases from 160°C to 220°C, yield stress decreased monotonically with processing temperature from 37±6 MPa to 19±4 MPa due to the increased thermal degradation of soy flour. Tensile modulus and strengths were adversely influenced by increasing soy content, but the strain-to-failure was not significantly affected. The inclusion of soy at 15 wt% resulted in fibers with a tensile modulus of 914±164 MPa and a tensile strength of 74±7 MPa, compared to neat PP fibers with a tensile modulus of 1224±136 MPa and a tensile strength of 104±10 MPa. Based on experiments conducted at different processing temperatures and different soy contents compositions, a spinning temperature of 190°C and a soy content of 15 wt% provided a good combination of ease of processability and adequate retention of tensile

properties by the blend. Increasing soy flour content led to bio-composite fibers with improved hydrophilic characteristics.

Finally, in Chapter 4, unlike the synthetic PE and PP that is non-biodegradable, PLA, a biodegradable resin, was used to process degradable soy-PLA fibers. Because PLA fiber spinning is much more difficult and fibers are much less ductile than its polyolefin counterparts, only 5 wt% soy could be incorporated in PLA matrix. Nonetheless, soy-PLA fibers were successfully melt-spun to prove the concept. As with polyolefin-based fibers, the soy-PLA fibers were found to have a rough surface (due to the presence of soy agglomerates) that reduces the plastic-like tactile feel. The tensile strength and modulus of soy-PLA fibers were lower than that of neat PLA, but the values of ~39 MPa and 1 GPa for tensile strength and modulus indicate the potential of such fibers for disposable nonwoven fabrics. More importantly, the presence of degradable soy filler contributed to the overall acceleration of hydrolytic degradation of PLA composite fibers by providing increased surface area. Thus, results from this chapter have established the feasibility of melt-spinning of soy-PLA fibers for potential use in bio-based nonwoven fabric applications requiring fast degradation.

5.2 Future Work

More sophisticated mixing studies that include dispersive processing elements and different mixing speeds may be conducted to further optimize the soy particle distribution in the polymer matrices. Also, a mixing speed of 100 rpm was chosen because DSM Microtruder has a maximum speed limit that is close to 100 rpm. A larger compounder can be used for higher-speed mixing studies to achieve better soy dispersion.

Although good mechanical properties were obtained in this study, the bonding between filler and matrix was primarily mechanical. To achieve better interfacial adhesion, different compatibilizers may be used in the blends, particularly for PLA base polymer to increase the soy content beyond 5 wt%. Then, a comparative study for the mechanical properties should be conducted as a pre-commercialization step for these biocomposite fibers.

Although the spinnability of soy-filled melt-spun polymer fibers with enhanced hydrophilicity and degradability has been established, processing of nonwovens by a continuous process such as patterned-roll calendaring, chemical bonding, and needle punching have not been investigated. It is important to note that the focus of this study was fiber processing and characterization, so it may be recalled that non-wovens in the current study were prepared only by lab-scale thermal bonding. Thus, the properties of the non-wovens resulting from the continuous processes should be measured for further studies. Hydrophilic properties should also be measured for the resulting non-wovens.

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