

Development of Soy Protein Plastics Using Functional Chemistry for Short-Life Biodegradable Applications

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ABSTRACT: Soy protein plastic formulations were developed through iterative experimental stages to produce water-stable, soy protein isolate (SPI)-based plastic resins. The protein polymer-based materials are glycerol and water plasticized resins that have been described as thermoplastics [1] by some researchers and have been described as materials that behave similar to thermoplastics upon application of heat and pressure [2]. Previous researchers have developed SPI plastic for various applications, all of which were adversely effected by water absorption. The formulations in this research included anhydride chemistries, such as maleic anhydride (MA), phthalic anhydride (PA), and bifunctional chemistries, such as adipic acid in combination with glycerol as plasticizer. The mass content of the respective functional chemistries were varied between 3 and 10 w/w% (total mass). Formulations based on phthalic anhydride exhibited the lowest water absorption; in particular, PA10% formulation exhibited water absorption of 21% compared to 250% for the control formulation after 24 h of exposure to water. Anhydride-based formulations were characterized using Fourier transform infrared spectroscopy (FTIR) to verify the fundamental mechanisms of improved water stability. In addition, cotton-based composites were studied to enhance the mechanical strength. The inclusion of fiber reinforcements reduced the overall dry and wet state mechanical properties.

The addition of adipic acid (AA) to PA5% reduced the tensile strength by 10–40%, depending on adipic acid concentration which was varied from 1.23–10%. Other cost effective formulations were developed and studied with varying levels of soy protein isolate (SPI) and soy flour (SF), which is a relatively inexpensive component compared to isolates (<\$1/lb compared to \$2–3/lb). It was observed that the addition of 2.5% AA to a PA5% formulation with a 50:50 ratio of SPI: SF reduced water absorption from 36% to 17%.

KEYWORDS: Water stability, protein plastics, anhydrides, molding and bioplastics

1 INTRODUCTION

The need to develop sustainable energy sources and materials has become an important objective of many nations. This includes the reduction of their respective contribution to the global carbon footprint as well as the use of renewable resources. In addition, varying crude oil prices cause a corresponding price fluctuation of commodity resins such as polypropylene (PP), polyethylene (PE), and polystyrene (PS). The compounded effects of such volatile market trends and uncertainty of crude supply has facilitated and increased the market demand for renewable alternative materials, particularly the demand for commercially available

biopolymers. Commercially available, sustainable plastics are primarily polyesters synthesized from derived or naturally occurring sugars, starch plastics, and blends of both. Currently, the market is largely dominated by bio-polyesters derived from sugar fermentation or cultured microorganisms, which include polymers such as polylactic acid (PLA) and polyhydroxyalkanoate (PHA) polymers.

Other proposed candidates include protein polymers that are derived from soybeans (as well as other plants). Over the last two decades, a significant amount of research has been completed by researchers on soy protein-based plastic resins for commercial plastic application [1–8]. The recent announcement by the US military and considerations by the civilian US aviation industry regarding the use of biodiesel as a replacement for jet fuel may prove synergetic with commercialization of soy protein plastics, because soybean oil

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is a common feed stock for biodiesel and one of the co-products of biodiesel production is soy protein in the form of soy flour (SF) and soy protein isolate (SPI). Thus, this may result in highly competitive prices and viable feedstock for bioplastics based on plant proteins. The utilization of these co-products also improves the efficiency of the biofuel process, thus reducing their processing and raw material cost. Addressing cost, which is one of the issues of soy-based plastics, at a recent United Soybean Board conference, it was reported that effectively designed soy plastics can be cost competitive with petroleum plastics such as polyethylene [9]. The estimates indicate that the inclusion of soy flour reduced formulation costs by 40% from \$1.29 to \$0.75 per pound as indicated in Table 1. It is important to note that the detailed costs only correspond to producing pellets and do not include net-shape forming operations, such as extrusion or injection molding.

An obstacle for the commercialization of soy protein-based plastics has been its sensitivity to moisture, which is a property caused by the hydrophilic nature of reactive groups on the surface and center structures within the protein molecule [3, 10]. A significant amount of prior research efforts have focused on addressing this issue by co-blending soy protein with biopolyesters [11, 12]. In contrast, the research work discussed in this article approaches the water sensitivity issue by using anhydrides and bifunctional/dicarboxylic acid chemistries that react with the hydroxyl functional groups on the protein molecules. Additionally, various fiber additives, such as cotton and sisal, were used as mechanical fillers to reduce the soy raw polymer content and increase the mechanical properties of the soy protein plastic resins.

The water sensitivity of soy protein plastics can be explained by the composition of SPI, the primary

substrate used for this work, which contains > 90% protein w/w%. Soy protein isolate, which is a mixture of two major protein subfractions, namely 11 S and 7 S, is hydrophilic in nature. The average molecular weights of the subfractions 11 S and 7 S are 350,000 kDa and 200,000 kDa, respectively [13]. Eleven (11) S, the higher molecular weight fraction, is a relatively hydrophobic protein in comparison to 7 S because of its functional side group configuration. However, the 7 S protein molecule constitutes approximately 70% of the total protein content of SPI. Thus, the overall property of SPI is hydrophilic [3, 14]. Previous researchers have utilized plasticizers such as glycerol and water as a solvent to produce SPI-based plastic resins [5–8,10]. Further developments involved blending of SPI plastic resins with biodegradable polyesters, such as Biomax and ϵ -polycaprolactone (PCL) to improve the mechanical properties and reduce moisture sensitivity [10, 11].

In the work presented here, chemicals that react with the hydrophilic structures were used. Initially, we used maleic and phthalic anhydride, which were chosen particularly for their bifunctional carboxyl side groups that would cause esterification with the hydroxyl functional groups on the protein structure during extrusion [7]. It was theorized that anhydride functional molecules, which exhibit high affinity for hydroxyl groups, would react with the hydroxyl sites on the protein molecule and reduce the hydrophobicity. The decrease/conversion of the hydroxyl reactive sites on the protein molecule would reduce the protein's affinity for water. In addition, it was expected that these chemistries would allow partial crosslinking of protein molecules. Other chemical reagents that were used included potassium phosphate (dibasic), a general anticoagulant [15]. It was theorized that the

Table 1 Cost comparison of anhydride soy resin formulations (PA 5%) with SPI and mixture of SPI and SF (50:50) as the raw resin.

Standard Soy protein isolate formulation (PA 5%)					Soy protein isolate and Soy flour formulation				
Ingredients	Parts	% Weight Fraction	\$/lbs	Price	Ingredients	Parts	% Weight Fraction	\$/lbs	Price
SPI	100	52.2	2.36	\$1.23	SPI	50	26.11	2.36	\$0.62
Glycerin	22.5	11.7	0.1	\$0.01	Soy flour/meal	50	26.11	0.28	\$0.07
PA	7.5	3.9	1.1	\$0.04	Glycerin	22.5	11.75	0.10	\$0.01
Water	60	31.3	0	\$0.00	PA	7.5	3.92	1.10	\$0.04
Sodium sulfite	1	0.5	0.9	\$0.00	Water	60	31.33	0.00	\$0.00
Potassium sorbate	0.5	0.3	0.31	\$0.00	Sodium sulfite	1	0.52	0.90	\$0.00
					Potassium sorbate	0.5	0.26	0.31	\$0.00
Total formulation Cost/lb	191.5	100		\$1.29		191.5	100		\$0.75

use of anticoagulants would prevent protein from refolding after swelling and unfolding induced by salts, solvents and mechanical shear in the extruder. The simultaneous use of anhydrides would increase the latter's reactive efficiency with the hydrophilic protein side groups. Food antioxidants, such as butylated hydroxy anisole (BA) [16], were also studied to determine their effects on the overall hydrophobicity of soy plastics. In order to increase the strength of our formulations, bio-fillers such as cotton fibers were used.

In order to assist plasticization of protein polymer, all formulations used sodium sulfite to cause cleavage of the cysteine links and promote unraveling of the protein structure in addition to glycerol and water [17]. The cysteine linkage is the naturally occurring crosslink in soy proteins that holds the secondary and tertiary protein structures in a globular conformation. Based on initial results, other dicarboxylic acid reagents were studied, such as adipic acid (AA) to promote crosslinking between the carboxyl groups [18] and enhance the mechanical properties of soy plastics. It was theorized that the use of AA in combination with PA would promote a polycondensation reaction of the hydroxyl side groups.

Because the concentration of soy protein isolate greatly affects the cost of the formulations, variants were developed with ratios of SPI and defatted soy flour (SF) along with various levels of fiber additions, e.g., sisal staple fibers which were utilized as mechanical fillers to reduce cost and improve mechanical properties. Using soy concentrate as an alternative raw polymer feedstock to SPI, screening experiments (results not detailed in this paper) indicated that soy-concentrate-based formulations produced inferior wet state properties compared to SPI: SF mixtures for plastic formulations.

2 MATERIALS

Soy protein isolate (SPI, ~90% protein) and soy flour were obtained from Solae Company, St. Louis, MO. Soy flour was selected as the polymer feedstock because of its relatively low cost compared to soy protein isolate. Plasticizer, in this case glycerol, salts, i.e., sodium sulfite (SS), potassium sorbate (KS), and potassium phosphate dibasic (DPP), were obtained from Fisher Scientific (Pittsburgh, PA). Maleic anhydride (MA), phthalic anhydride (PA), butylated hydroxy anisole (BA), and adipic acid (AA) were procured from Sigma Aldrich and Acros Organics. Phthalic anhydride, adipic acid and butylated hydroxy anisole were used to reduce protein polarity and promote molecule to molecule crosslinking with the final goal of achieving a water stable structure. In addition, sodium sulfite

and potassium phosphate dibasic were studied to promote protein denaturing (unfolding) to enhance extrusion processing. Potassium sorbate was used as an antifungal and antimicrobial agent. Glycerol was selected as a plasticizer because of its abundance and low price as a co-product from the biodiesel industry. Cotton fiber (Cf) was prepared by cutting mercerized cotton yarn (from local sources) hank to 19 to 25 mm lengths, followed by fluffing to individualize the fibers. Cotton powder (Cp) was obtained from Northern Technologies Inc., MN. Sisal fibers were obtained from a local source in the form of low twist twine, which was chopped with a cutting mill to 12 mm lengths. While longer fibers (19–25 mm) were desired for the sisal fibers to enhance better load transfer between the resin and the fiber, the stiffness of the fibers prevented proper mixing and extrusion and the maximum length of the sisal fibers was limited to 12 mm.

3 METHODS

3.1 Preparation and Processing

The experimental plan was divided into three separate tasks. In Task 1, screening experiments were conducted with SPI as the raw polymer to determine which anhydride reagents enhanced water stability and wet-state mechanical properties of soy protein plastic resins. Further, cotton fibers and fine powder were included in the initial formulations to verify enhancement in mechanical properties of the resulting soy plastic resins. In Task 2, formulations from Task 1 with improved water stability were investigated for further improvement of wet-state properties, utilizing adipic acid (AA) as an additional agent. In Task 3, with the objective of reducing the cost of formulated resin, the formulations with best results from Task 1 and 2 were further modified, utilizing defatted soy flour (SF) to replace the relatively high-priced soy protein isolate (SPI) as the raw polymer. Each of these tasks is detailed in the following sections.

3.1.1 Task I

Based on initial trials and literature review, various chemical reagents utilized for screening experiments were based on acid anhydride. Each formulation, including the control formulation, consisted of a solid fraction with 100 parts (1 kg) of SPI and a liquid fraction containing water, glycerol, SS, KS, and the respective chemistries for each formulation (except the control formulation), as detailed in Table 2. The liquid fraction for each formulation was prepared by mixing a solution of the salts in water and the respective

Table 2 Component matrix for stage I plastic formulations (chemical additives only).

Component Formulation	Base Solution								
	SPI	Water	SS	KS	Glycerol	MA	PA	BA	DPP
Control	100	65	0.5	0.5	30	–	–	–	–
MA 3%	100	65	0.5	0.5	25.5	4.5	–	–	–
MA 5%	100	65	0.5	0.5	22.5	7.5	–	–	–
PA 3.5%	100	65	0.5	0.5	24.7	–	5.3	–	–
PA 5%	100	65	0.5	0.5	22.5	–	7.5	–	–
PA 10%	100	65	1	0.5	15	–	15	–	–
BA 0.5%	100	65	0.5	0.5	30	–	–	0.7	–
D+PA 5%	100	65	0.5	0.5	22.5	–	7.5	–	1
D+PA 10%	100	65	0.5	0.5	15	–	15	–	1

Numbers in the table represent the mass of respective component measured in parts with respect to 100 parts of SPI.

*SS-sodium sulfite, KS-potassium sorbate, MA-maleic anhydride, PA-phthalic anhydride, BA-butylated hydroxy anisole, DPP-potassium phosphate dibasic

chemistries in glycerol, which were combined prior to mixing with SPI. In order to keep the SPI concentration constant for all formulations, the overall additive contribution was maintained at 30 parts for all formulations. For various formulations with different levels of chemical additives, the glycerol content was varied (increased or decreased) accordingly to maintain a constant additive contribution. Each formulation was prepared by mixing the solid and liquid components in a high speed mixer (Henschel Mixers American, Inc., Houston, TX) at 2000 rpm to produce a resin with the consistency of dough. The liquids were added to the mixer containing the SPI at a slow rate to avoid lump formation and to achieve uniform mixing. With composite plastic formulations, fillers such as cotton fibers (Cf) and cotton powder (Cp) were mixed with SPI prior to mixing with the liquid fraction, as detailed in Table 3. These formulations were prepared following the same procedure as discussed for anhydride plastics formulations, where the anhydride chemistry also functioned as a coupling agent. For the phthalic anhydride (PA10%) formulation, one (1.0) part of sodium sulfite (SS) was used instead of the standard 0.5 parts in order to facilitate better protein unfolding and to increase the exposed protein surface area. As detailed previously, the increase in protein surface area exposes more hydroxyl groups and thus enhances the probability of reaction between the anhydrides and the hydroxyl sites on the protein. The liquid and dry mixtures of the respective formulations were further extruded on a Leistritz compounding twin-screw extruder (Leistritz Micro18, L/D ratio 30, American Leistritz Corp., Somerville, NJ) to produce plastic extrudate

Table 3 Component matrix for stage I composite plastic formulations (chemical, fiber, and particulate additives).

Component Formulation	SPI	Base chemical formulation	Cf	Cp
C _f	100	Control	2	–
C _f MA 3%	100	MA 3%	2	–
C _f PA 5%	100	PA 5%	2	–
C _f PA 10%	100	PA 10%	2	–
C _p	100	Control	–	20
C _p PA 10%	100	PA 10%	–	20

Numbers in the table represent the mass of respective component measured in parts with respect to 100 parts of SPI.

*Cf-cotton fiber, Cp- cotton powder.

that was pelletized with a pellet mill (Scheer Bay Inc., WI). The temperature profile during extrusion increased from 95 to 110°C from the hopper to the die for all formulations, except for phthalic anhydride formulations, which ranged between 95 and 125°C. The pellets were conditioned to a final moisture level of 10–15%, depending on the various formulations and were further injection molded using a 22 S Boy machine (20 ton clamping force) into ASTM 638 standard tensile test samples. The injection molding was completed at temperatures between 120 to 135°C for all formulations, except maleic anhydride formulations, which were molded at 110 to 120°C.

It is important to note that the formulation with 10% of MA was not included in the investigation because the resulting extrudate exhibited degradation and less structural integrity and the material was not processable by injection molding. Similarly, formulation variants of DPP with MA5% and MA10% were not included in the investigation because of the low structural integrity and degradation observed in the extrudate.

3.1.2 Task II

Because formulations based on PA5% exhibited enhanced mechanical and water resistance properties compared to other formulations, they were selected as base formulations. To further promote polycondensation reaction, adipic acid (AA) was used in various concentrations as another dicarboxylic functional chemistry in addition to phthalic anhydride (PA), as detailed in Table 4. The sample preparation of formulations based on AA with PA was completed following the same procedures as for the PA5% formulation. It is important to note that the effects of adipic acid without PA on the mechanical and water absorption properties of soy protein plastics were studied in screening experiments and because no significant improvements were observed, those results are not reported here.

3.1.3 Task III

Based on the formulations identified in Tasks I and II, additional formulations were studied with less costly base ingredients, namely soy flour (SF) instead of SPI. In addition, the inclusions of fillers to enhance mechanical properties, such as sisal staple fibers (12 mm long) were also studied, as detailed in Table 5.

Table 4 Component matrix for stage II plastic formulations (chemical additives).

Formulation \ Component	SPI	Base chemical formulation	AA
AA 1.23%	100	PA 5%	1.85
AA 2.5%	100	PA 5%	3.75
AA 5%	100	PA 5%	7.5
AA 7.5%	100	PA 5%	11.25
AA 10%	100	PA 5%	15

Numbers in the table represent the mass of respective component measured in parts with respect to 100 parts of SPI.

*AA-adipic acid.

Table 5 Component matrix for stage III plastic formulations (chemical and fiber additives).

Formulation \ Component	SPI: SF	Base chemical formulation	Sisal staple fiber
A	75:25	PA 5%	–
B	75:25	PA 10%	–
C	50:50	PA 5%	–
D	50:50	PA 10%	–
A1	75:25	PA 5%	2.5
A2	75:25	PA 5%	7.5
A3	75:25	AA 2.5%	–
B	75:25	PA 10%	–
B2	75:25	PA 10%	7.5
B4	75:25	AA 5%	–
C3	50:50	AA 2.5%	–
D4	50:50	AA 5%	–

Numbers in the table represent the mass of respective component measured in parts with respect to 100 parts of soy protein polymer.

3.2 Testing and Evaluation

3.2.1 Dry state tensile strength testing

The dry state tensile strength of samples from various formulations was determined following ASTM 638 D procedures. The tensile testing was conducted utilizing an Instron tensile frame (Model 4502, Instron Corporation, Canton, MA) with a crosshead speed of 5 mm/min. A population size of seven samples was tested for each formulation. All samples tested were conditioned by open-air drying for a period of 24 h prior to testing.

3.2.2 Water absorption testing

All sample formulations were tested for water absorption in accordance with ASTM D570–98. The samples were conditioned by open-air drying for a period of 24 h prior to immersing them in distilled water. Water absorption levels of the samples were measured every 2 h over a time period of 24 h for duplicate sets. The water absorption value (WAV) was determined by calculating the difference in weight between the initial dry and wet samples and expressed as percentage over the dry weight of the sample.

3.2.3 Wet-state tensile strength testing

Samples were tested for tensile strength in wet-state conditions following ASTM D638–08. The number of samples utilized for wet-state characterization (both

water absorption and wet-state strength) was limited to two samples per data point because of the low volume capacity of the high speed mixer, resulting in a restricted number of samples moldable from the respective formulation batch (21 samples/batch).

3.2.4 Fourier transform infrared spectroscopy (FTIR)

In order to confirm the theoretical chemical reactions proposed in this work, both phthalic and maleic anhydride formulations were characterized using FTIR. The characterizations were completed with mid-IR wave numbers ($500\text{--}4000\text{ cm}^{-1}$), with cesium iodide as background material.

4 RESULTS AND OBSERVATIONS

Soy plastics compounded with phthalic anhydride exhibited higher dry-state tensile strength relative to other anhydride and composite formulations as seen in Figure 1. The tensile strength of PA 5% was 8.4 MPa, which was the highest strength among Task I formulations and thus was selected as the base for formulation development in Tasks II and III. The addition of fiber and powder additives reduced the dry state strength, which was attributed to inefficient coupling between the polymer matrix and the additives. The injection molded PA formulation samples were brittle after the conditioning process. The material was also difficult to reprocess because of its brittleness, suggesting intermolecular bonding caused by phthalic anhydride in the soy polymer matrix. This theory was reinforced by results from FTIR (further detailed in the following

section) analysis that confirmed the formation of new amide linkages with the addition of PA. Soy plastics compounded with maleic anhydride exhibited better water resistance in comparison with the control formulation that had no chemical additives or inclusions. The water resistance of soy plastics was generally proportional to the concentration of maleic anhydride, as seen in Figure 2. For the maleic anhydride formulations (MA 3% and MA 5%), water absorption after 24 h was reduced from 70% to 27%. For phthalic anhydride formulations (PA 3.5%, 5%, and 10%), water absorption of the plastics followed a similar trend. The formulation with PA 10% exhibited water absorption of 21% after 24 h, which was the lowest among the anhydride plastic formulations, as seen in Figure 2.

These results are in agreement with the theory that anhydrides have an affinity for hydroxyl groups on the protein, consequently making the protein less hydrophilic. This is also in agreement with the theory that using anhydrides as reactants will promote water stability or hydrophobicity of soy plastics. While processing of SF typically results in discoloration and odors, these effects were not seen with the majority of the formulation studied here, and it is believed to be the result of chemistries that were used to enhance processability. In more detail, the protein structure was denatured from a globular structure to a more linear structure, allowing it to be processed with less pressure and shear reducing molecular degradation. The formulation with BA 0.5% exhibited some improved water stability, but it was not as significant as the improvements seen with anhydride formulations. Formulations based on dibasic potassium salt

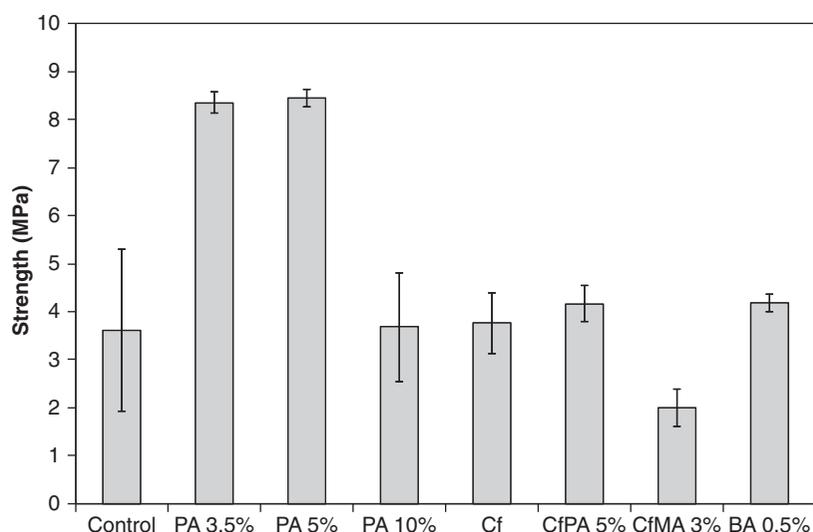


Figure 1 Dry state strength of phthalic anhydride and composite soy plastic resin formulations.

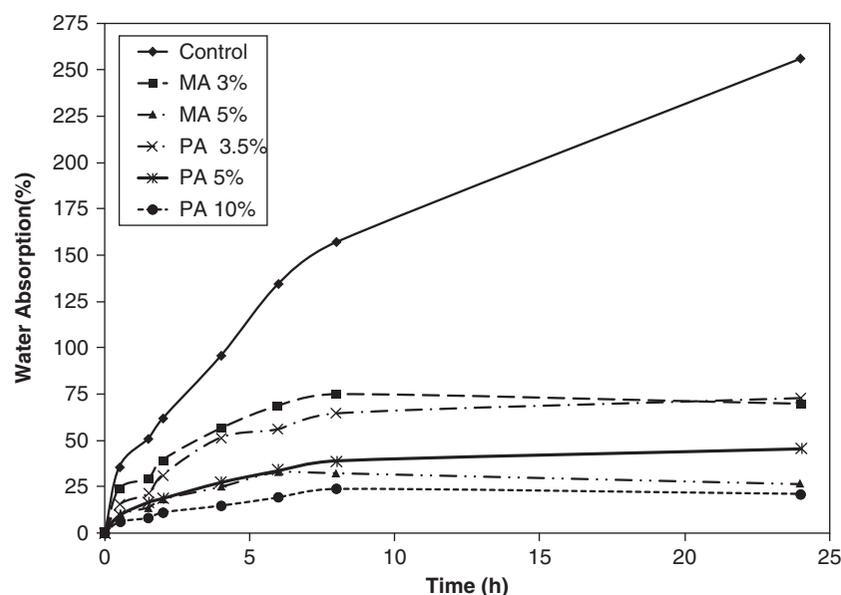


Figure 2 Water absorption of maleic and phthalic anhydride formulations over 24 h of exposure to water.

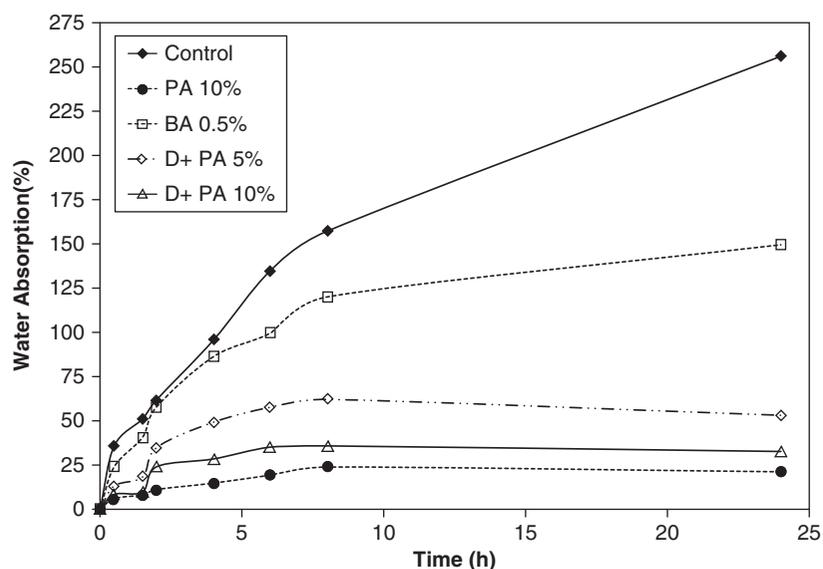


Figure 3 Water absorption for soy plastics resin formulations with antioxidant additives and anhydride with salts over 24 h.

(D) with phthalic anhydride D+PA 5% and D+PA 10% exhibited higher water absorption values in comparison with the respective phthalic anhydride formulation, as seen in Figure 2.

Following the water absorption test, FTIR characterization was conducted for the control, the PA 10%, and the MA 5% formulations, because they exhibited in the lowest water absorption values. Figure 3 shows that the FTIR spectra for control and anhydride formulations exhibited common peaks at wave number positions of 1672, 1545, and 1254 cm^{-1} , corresponding to amide I (C=O), amide II (N-H), and amide III (C-N and N-H)

bond vibrations in the soy protein molecule, respectively [19]. Other common features were the broad peak from 3200–3600 cm^{-1} , corresponding to the free and bounded -OH and -NH groups on the protein surface [16] and peaks at 1063 and 1118 cm^{-1} corresponding to the vibrations of C-C and C-OH bonds present in the glycerol molecule [13, 20]. Distinct peaks at 868 cm^{-1} and 723 cm^{-1} for MA 5% and PA 10% are representative of the C-H bonds situated on the opened ring of the maleic anhydride molecule (derived from an aromatic source) and C-H bonds on the aromatic ring of the phthalic anhydride molecule, respectively [21].

A twin peak at 1718 cm^{-1} exhibited by both PA 10% and MA 5% spectra suggests the formation of new, saturated carboxylic acid side groups and reformation of amide I bonds [16]. In addition, positional shift and change in the shape of the amide III peaks for MA 5% and PA 10% at 1254 cm^{-1} indicate reformation of amide linkages resulting from interaction with anhydrides and other side groups as a result neutralizing the polar linkages in the secondary structure of the protein [16, 22]. Thus, based on the results of the FTIR analysis, water absorption testing and the brittle nature of the resulting resin, it is believed that the chemical reactions with the anhydride molecules did improve water stability of soy protein-based plastics through ester formation and crosslinking of free reactive sites. Although the mechanism of stabilization was crosslinking, the viscoelastic behavior of the resulting plastic suggested that the degree of crosslinking was not high enough to result in a rigid thermoset. While the FTIR supports the formation of ester linkages as postulated, it does not provide insight into the completion of the reaction and presence of residual unreacted materials. The observation suggested that the crosslinking caused by anhydrides was restricted to the surface of the protein molecule and contributed little to strengthening the protein molecule. This hypothesis was supported by the low wet-state mechanical properties observed.

Composite plastic formulations using cotton fiber (Cf) and cotton powder (Cp) in combination with anhydrides exhibited marginally better water resistance properties compared to net anhydride plastics formulations. In Figure 4 it is seen that

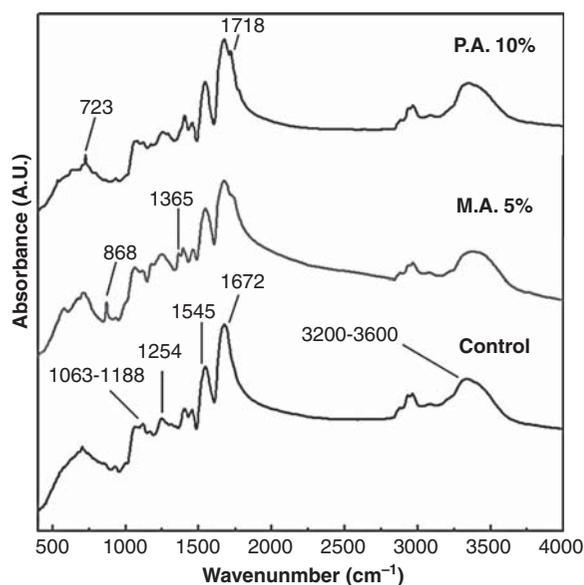


Figure 4 FTIR absorbance spectrums for control, MA 5% and PA 10% formulations.

the formulations Cf and Cp exhibited less water absorption compared to the control samples. Cotton fiber and powder with phthalic anhydride formulations (Cf PA 10% and Cp PA 10%) exhibited water absorption values of 19.0% and 16.8% after 24 h, respectively, as seen in Figure 5. It was noted that wet strength of all formulations dropped below 1 MPa within the first 5 h of submersion in water, except for formulations PA 10% and Cf PA 10%. It is believed that the addition of particulates and fibers created a mechanical water barrier and formed a composite structure that reduced the rate of water diffusion through the plastic matrix. The objective of improving wet state strength with the addition of particulates was partially achieved, as seen in Figure 6. The strength was maintained for the initial 1 to 2 h of the test. After 24 h, the wet strength of

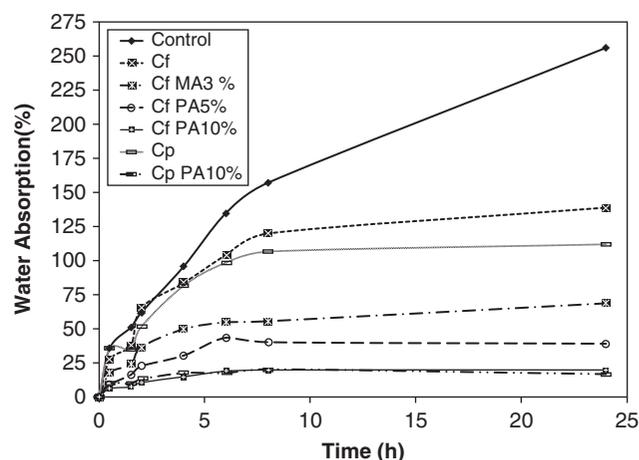


Figure 5 Water absorption of soy plastics resin formulations with cotton fiber and cotton powder over 24 h of exposure to water steeping.

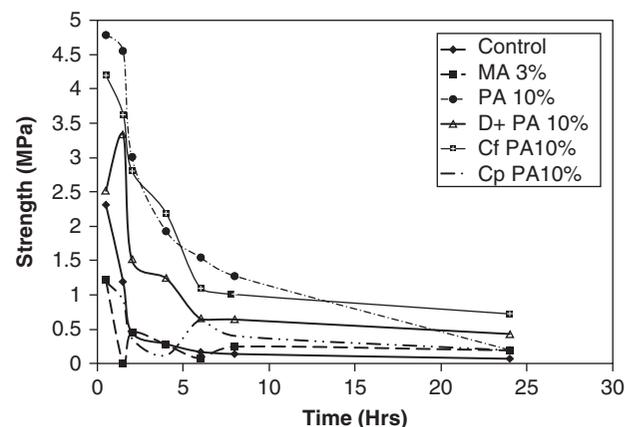


Figure 6 Wet state tensile strength at intermittent intervals over 24 h of exposure to water.

particulate reinforced formulations was only marginally better than the formulations without the particulate additives. It is believed that while the cotton reinforced the composite, the matrix (protein polymer) was weakened by the water, preventing load transmission to the fibers and resulting in a reduction in strength of the composite.

With respect to Task II, adipic acid (AA) formulations (with PA 5% as base material), the dry-state tensile strength decreased with increasing concentration of AA, as depicted in Figure 7. The overall decrease in mechanical properties was unexpected. It was theorized that the increase in adipic acid concentration (a six carbon linear bifunctional chemistry in contrast to a stiffer ring molecule, such as phthalic anhydride) may have rendered the reacted

protein polymer with a certain degree of molecular flexibility and consequently reduced strength. The wet-state tensile strength and water absorption values for AA formulations were reduced at lower concentrations (0 to 2.5%) of AA; however, they improved with higher AA concentration (5 to 10%, with respect to control), as seen in Figure 8. It was seen that the increase in concentration of adipic acid was inversely related to the wet-state and dry-state properties of AA-based plastic formulations.

Task III formulations, in which SPI and SF were utilized in different ratios as the raw polymer, exhibited 50% lower tensile strength values compared to formulations based on 100% SPI, as seen in Figure 9. The overall reduction in strength can be attributed to the high carbohydrate content (40%) of soy flour compared to that of SPI (4–6%). The presence of carbohydrate resulted in high moisture absorption and reduced strength values because of the hydrophilic nature and smaller molecular size of carbohydrates compared to proteins. As seen in Figure 10, the moisture absorption values of SPI: SF formulations are higher compared to the respective anhydride formulations with 100% SPI. The water absorption profiles of SPI: SF formulations with AA and sisal fibers are not reported here because their performance was inferior.

The water absorption values for PA 5% SPI: SF [50:50] formulations decreased from 36% to 17% with the addition of 2.5 w/w% of AA, as seen in Figure 11. Based on these results, PA 5% SPI: SF [50:50] formulations were chosen for an in-depth evaluation as biodegradable materials for plant pots, the results of which will be discussed in a future paper (Part 2).

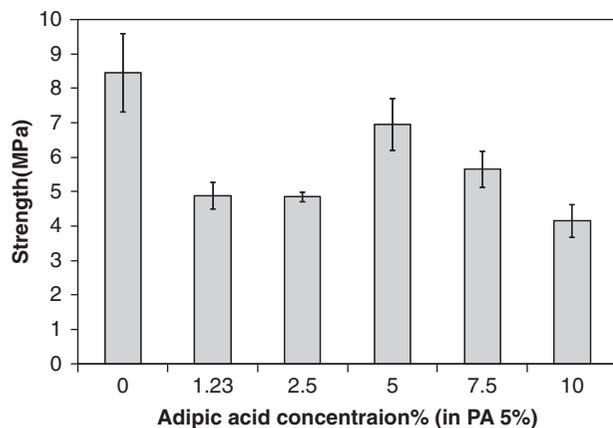


Figure 7 Dry state strength of adipic acid based soy plastics resin formulations with PA5% as the base material.

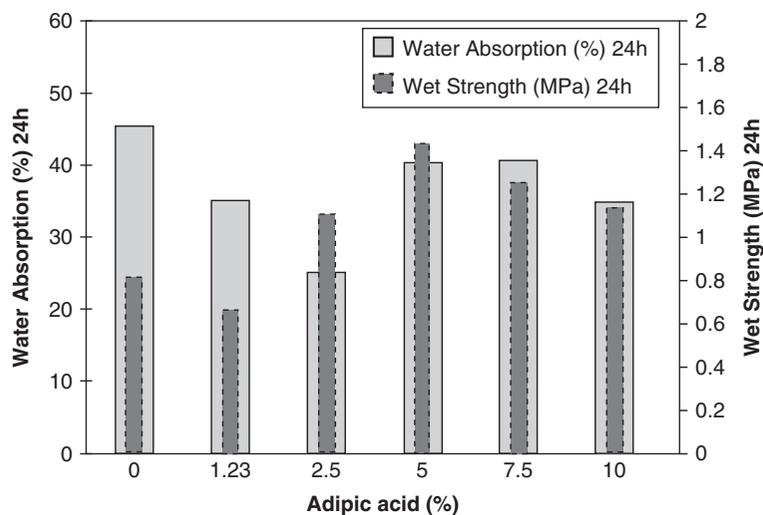


Figure 8 Water absorption and wet strength of adipic acid based soy plastics resin formulations with PA5% as the base material.

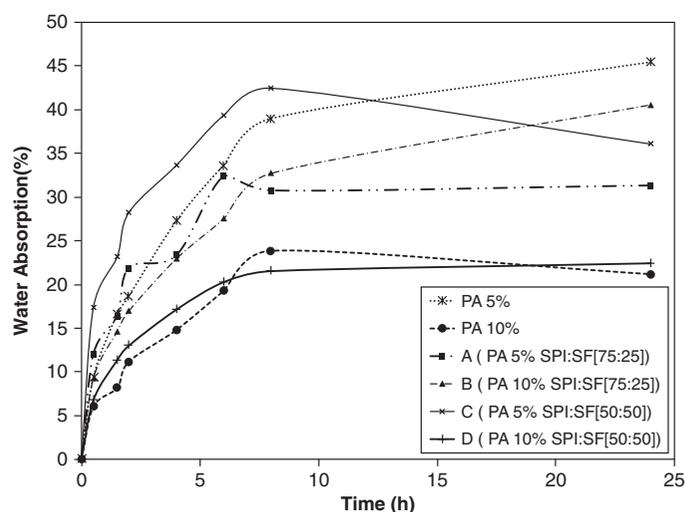


Figure 9 Dry state strength of phthalic anhydride based soy protein isolate: soy flour formulations.

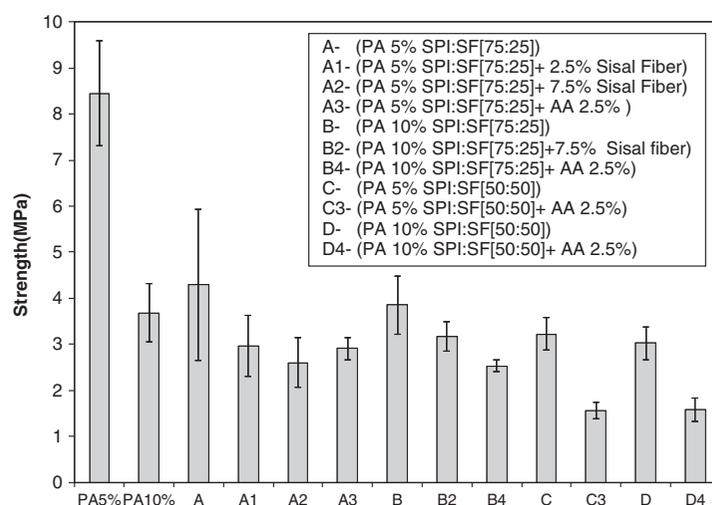


Figure 10 Water absorption of phthalic anhydride based soy protein isolate: soy flour formulations, 24 h of exposure to water.

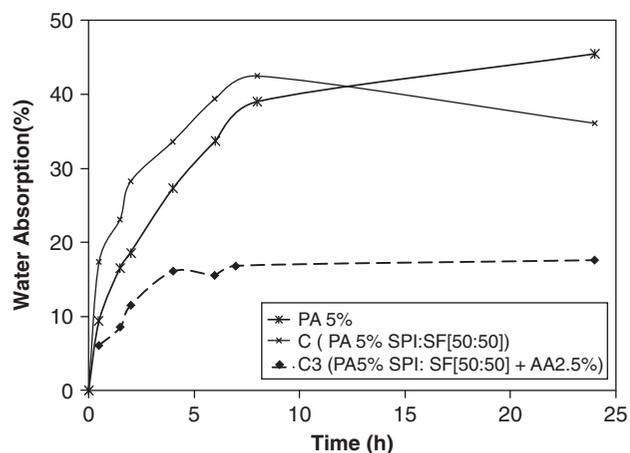


Figure 11 Water absorption of PA 5% formulation compared with corresponding 50:50- SPI : SF based plastic formulations over 24 h of exposure to water.

4 CONCLUSION

Water absorption properties of soy protein-based plastics can be improved by reacting anhydrides with the hydrophilic groups on the protein molecule. The results of the FTIR studies were in good agreement with the theory that the anhydrides react with and bond to the hydroxyl reactive sites on the protein molecule, making the protein polymer less hydrophilic. The mechanical properties were modified by using additives, such as cotton fibers and cotton powder. Even though water absorption properties of soy protein plastics were similar to some commercial polyamides, the wet-state mechanical strengths were low. The tensile strength properties of anhydride-based formulations were further modified using dicarboxylic/bifunctional acids, such as adipic acid, and by changing the soy polymer composition. The use of soy flour as the raw polymer

feedstock reduced the tensile strength properties, but rendered water absorption properties similar to 100% SPI anhydride-based formulations.

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