

## Development and Characterization of Plasticized Starch-Based Biocomposites with Soy Pulp as Reinforcement Filler

Ajaya Kumar Behera,<sup>1</sup> Sridevi Avancha,<sup>1</sup> Ramkrishna Sen,<sup>2</sup> Basudam Adhikari<sup>1</sup>

<sup>1</sup>Materials Science Centre, Indian Institute of Technology Kharagpur, West Bengal 721302, India

<sup>2</sup>Department of Biotechnology, Indian Institute of Technology Kharagpur, West Bengal 721302, India

Correspondence to: R. Sen (E-mail: rksen@yahoo.com)

**ABSTRACT:** Soy pulp, a byproduct of soymilk industry, was used in varying amount as reinforcement filler with thermoplastic starch, to develop and characterize starch–soy (SS) composites. The composite filled with 10 wt % soy pulp showed 112% and 98% increment in tensile and flexural strength, respectively. Fourier transform infrared spectrum of composite revealed occurrence of chemical bonding between hydroxyl group of soy pulp and that of starch matrix. The optimized composite containing 10 wt % soy pulp, with maximum mechanical strength was found thermally stable up to 312°C. Water absorption of these composites was enhanced with the increase in filler loading due to increase in hydrophilicity as evident from lowering of contact angle value. These composites are expected to be ecofriendly as soy pulp and starch are biodegradable in nature. The SS pulp composites so developed and characterized find potential application as disposable and packaging items. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** biocomposite; soy pulp; characterization; thermal analysis; water absorption

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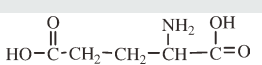
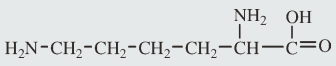
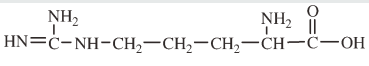
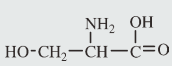
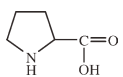
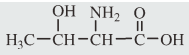
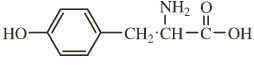
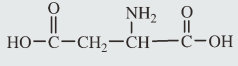
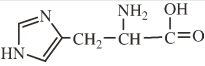
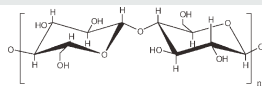
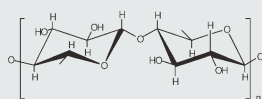
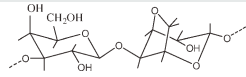
### INTRODUCTION

Research and development in the field of sustainable composites are growing day to day with fruitful outcome.<sup>1</sup> Many researchers have utilized traditional filler like nanoclay, kaolin, talc, etc., with thermoplastic/thermoset to prepare physically and mechanically stronger composite than the base polymer.<sup>2,3</sup> However, the biodegradability of these composites is of great concern as both matrix and filler materials are not degradable in soil bed, hence contributes to environmental hazard. To replace traditional fillers, agrofillers are being utilized as reinforcing material along with thermoplastic/thermoset resin to produce sustainable fiber reinforced as well as particle reinforced composites. This has led for development of biocomposites using biodegradable fillers like lignin, cellulose, wood flour (WF), rice husk flour (RHF), etc., with thermoplastic/thermoset resins to meet the criterion of sustainable composites.<sup>4,5</sup>

The biofillers in composite offer a number of lucrative advantages viz., low cost, low density, high specific strength and stiffness, ecofriendliness, and biodegradability. Yang et al.<sup>5</sup> fabricated RHF and WF reinforced polypropylene (PP) and low-density polyethylene (LDPE) composites. Thermal stability of these composites decreased with increasing filler content as compared to the polymer matrix due to low thermal stability of the filler materials. Tensile strength of these composites decreased with

increase in RHF content due to poor bonding between hydrophilic filler and hydrophobic matrix.<sup>6</sup> In presence of compatibilizing agent, i.e., maleated polypropylene, tensile strength of above composites enhanced drastically as compared to that of neat polymer.<sup>7</sup> Carvalho et al.<sup>8</sup> developed thermoplastic starch (TPS)–clay composites using different weight percentages of kaolin (clay) as filler, and reported about increment of 50% in tensile strength for 50 phr filler loaded composites. This was obtained due to good interaction between starch and clay which also increased moisture resistance of the composite. Curvelo et al.<sup>9</sup> prepared thermoplastic corn starch composites with cellulosic fibers and reported about enhancement of 100% in tensile strength and 50% in tensile modulus for 16 wt % fiber loaded composite due to formation of hydrogen bonding between functional groups of polar matrix and polar filler material. Using wheat straw as lignocellulosic filler in polybutylene adipate-*co*-terephthalate (PBAT) matrix, Averous and Digabel<sup>10</sup> developed a new organic biocomposites and reported that loading of biofiller slightly enhanced both the tensile strength and thermal degradation temperature of the biocomposite. Zhao et al.<sup>11</sup> fabricated RHF reinforced poly(caprolactone) (PCL) composites and reported about their biodegradable nature. The presence of RHF accelerated the degradation of the PCL matrix in the composites, and this acceleration effect increased with increase in filler content.

**Table I.** Major Constituents of Soy Pulp

Constituents	Amount (%)
Soy protein	17–24
Glutamic acid	
Lysine	
Arginine	
Serine	
Proline	
Threonine	
Tyrosine	
Aspartic acid	
Histidine	
Soy and crude fibers	12–14.5
Cellulose	
Hemicellulose	
Arabinogalactan	
Fats	16–20

Soy pulp is a major byproduct of soymilk manufacturing industries. It is composed of soy protein, soy fibers (polysaccharides), and some fats. Polysaccharides include mainly cellulose, arabinan, arabinogalactan, and an acidic polysaccharide complex.<sup>12</sup> Some major soy proteins with structure are reported in Table I.<sup>12,13</sup> Different functional groups in soy pulp can interact with that of thermoplastic/thermoset matrix to result in making a strong composite.

In this work, TPS and soy pulp were utilized as matrix and reinforcing filler, respectively. TPS–soy pulp composites were fabricated using different weight percentages of soy pulp with the compatibilizing agent glycerol. Developed starch–soy (SS) pulp composites were subsequently characterized for their mechanical properties, contact angle (CA), water absorption capacity, and thermal stability. Fabricated composites composed of low cost, and biodegradable soy pulp are expected to be a good value added bioproducts which can be utilized in packaging and disposable items.

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## EXPERIMENTAL

### Raw Materials

TPS (derived from corn starch and blended with polyester) was supplied by Biograde (Nanjing) Pty, China. Soy seeds and Glycerol (Merck, India) were procured from local market.

### Preparation of Soy Pulp from Soy Seeds

Soy seeds were soaked in distilled water (1:4 w/v) for 4 h. Water soaked soy seeds were crushed using mixer grinder to prepare soy paste. Soy paste was squeezed through nylon cloth and filtrate was collected as soy milk. The water insoluble soy residue on nylon cloth was collected and dried at 60°C for 30 min and further crushed to reduce its mesh size (<50 μm). This solid soy extract (soy pulp) was kept at 80°C for over night in a vacuum oven to maintain <5% moisture content and then stored in a desiccant with sealed containers for further use.

### Fabrication of SS Pulp Composites

Blends with various amounts (0, 5, 10, 15, 20, and 25 wt %) of soy pulp with glycerol (5 wt %) and TPS were prepared by melt mixing at 100°C and 60 rpm for 5 min using an internal mixer having double screw extruder (Brabender mixing chamber).<sup>14</sup> These different sets of SS pulp blends were collected and then compressed in a hot press at the temperature of 105°C for 10 min under 6 MPa pressures to prepare SS pulp composites. Fabricated composites comprising 0–25 wt % soy pulp are coded as SS0–6, respectively.

### Sample Characterizations

Tensile and flexural measurements were carried out by following ASTM D638-03 and ASTM D790-03 methods respectively, using universal tensile testing instrument (Hounsfield HS 10KS, UK) at room temperature (RT). Tensile and flexural testing was carried out with an extension speed of 5 mm/min and 2 mm/min, respectively. Dumbbell-shaped test samples (64 × 12.7 × 3.2 mm<sup>3</sup>) were used for tensile testing. The tensile and flexural strength results reported are the averages of 10 samples for each composite.

To know the interaction between filler and matrix in composite, Fourier transform infrared (FTIR) analysis of TPS, soy pulp and SS2 samples with KBr pellets were carried out using a Thermo Nicolet, Nexus 870 IR spectrometer. The spectra were recorded from 400 to 4000 cm<sup>-1</sup>. Before making KBr pellet the composite powder was dried under vacuum at 60°C for 12 h.

The phase morphology of the SS composites (SS0, SS2, and SS5) was studied with a scanning electron microscope (SUPRA-40, Germany) instrument operated at an accelerating voltage of 5 kV. The composite specimens broken during tensile testing were coated with a thin layer of gold to prevent electrical charging, and FE-SEM images of fractured surfaces were taken.

To check water sensitivity of fabricated composites, CA measurement of SS composites were carried out using a SEO CA meter at RT (32 ± 1°C) and 75% relative humidity (RH). A

**Table II.** Mechanical Properties of Plasticized SS Composites

Specimens	PS (wt %)	SP (wt %)	TS ± SD (MPa)	TM ± SD (MPa)	EB ± SD (%)	FS ± SD (MPa)	FM ± SD (MPa)
SS0	100	0	3.31 ± 0.04	53.5 ± 4.31	8.78 ± 0.18	3.24 ± 0.03	54.2 ± 4.36
SS1	95	5	4.26 ± 0.03	67.9 ± 4.52	7.24 ± 0.22	4.02 ± 0.03	66.8 ± 4.43
SS2	90	10	7.02 ± 0.04	82.7 ± 4.78	6.82 ± 0.25	6.41 ± 0.04	76.5 ± 4.61
SS3	85	15	4.92 ± 0.04	60.2 ± 4.30	5.89 ± 0.24	3.79 ± 0.04	58.2 ± 4.37
SS4	80	20	3.68 ± 0.05	49.7 ± 4.51	5.32 ± 0.22	2.58 ± 0.03	46.9 ± 4.33
SS5	75	25	2.04 ± 0.06	44.8 ± 4.60	4.98 ± 0.12	1.86 ± 0.05	42.7 ± 4.28

PS, plasticized starch; SP, soy pulp; TS, tensile strength; TM, tensile modulus; EB, elongation at break; FS, flexural strength; FM, flexural modulus; SD, standard deviation.

drop of water (1–2 μL) was dropped on sample surface through a microsyringe and a photograph was taken for each test with CCD camera attached to the instrument. At least five measurements were taken from different areas on sample surface and average CA value was reported.

To check the dimensional stability in water, water sorption and thickness swelling of SS composites (specimen size of 90 × 60 × 6 mm<sup>3</sup>) were determined in distilled water at RT (32 ± 1°C) and 75% RH for 24 h, and in boiling distilled water for 2 h according to ASTM D570-05. At the end of each time period, five specimens of each composite were removed, gently wiped with tissue paper to remove the excess water on the surface and immediately weighed. Water absorption capacity (%) of the composites was calculated using the following formula:

$$\text{Water absorption (\%)} = 100 \times \frac{W_f - W_i}{W_i} \quad (1)$$

where  $W_i$  is the initial weight of the specimen before immersing in water, and  $W_f$  is the final weight of the specimen after specific time of immersion in distilled water. Similarly thickness swelling (TS) after end of the each time period was calculated using the formula:

$$\text{Thickness swelling (\%)} = 100 \times \frac{T_f - T_i}{T_i} \quad (2)$$

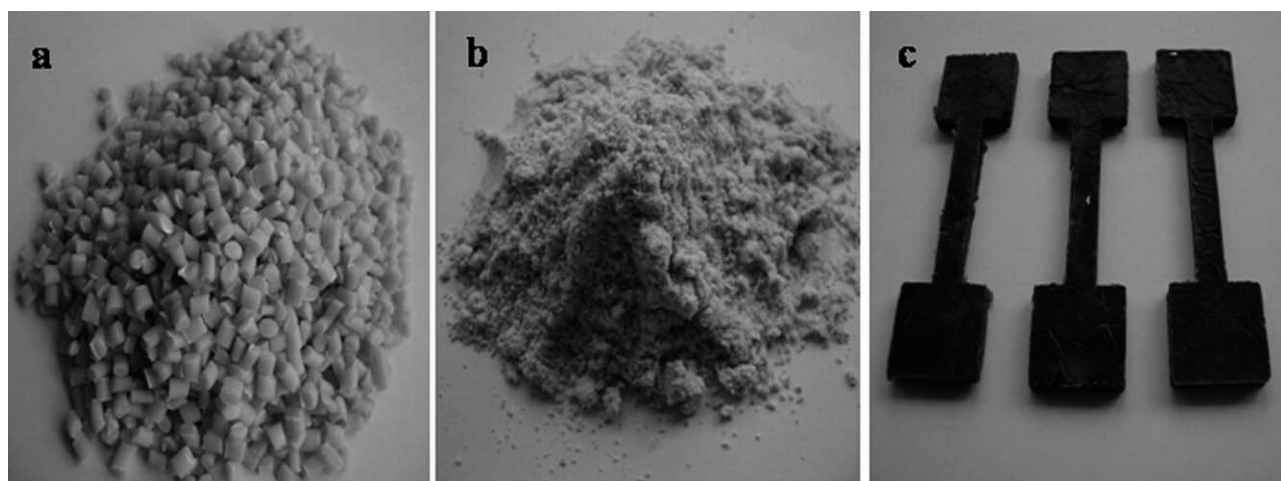
where  $T_i$  is the thickness of the specimen before immersing in water, and  $T_f$  is the final thickness of the specimen after end of the specific time.

The thermal stability (onset degradation temperature) of TPS, soy pulp, and SS2 composite was investigated with TGA (TGA-209F, Netzsch, Germany). The samples were heated in air atmosphere from 32 to 600°C at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Mechanical Properties of SS Composites

Mechanical properties of the composites of soy pulp and TPS are shown in Table II. The digital photographs of TPS, soy pulp, and tensile specimens of SS composites are illustrated in Figure 1. The tensile strength and modulus of SS composites increased with the increase in filler loading from 0 to 10 wt %. There was 112% increment in tensile strength and 54% in the tensile modulus of the composite containing 10 wt % soy pulp achieved. This increment in tensile properties of SS2 composite was due to the better interfacial bonding between soy pulp and the starch. Interfacial bonding obtained might be due to possible formation of hydrogen bonding between the hydroxyl groups of the matrix and amino or carboxyl groups of soy protein (filler). The physical entanglement interaction in form of possible chemical reaction or hydrogen bonding between the glycerol, soy pulp, and the TPS improved the compatibility of



**Figure 1.** Digital photographs of (a) TPS, (b) soy pulp, and (c) tensile specimens of TPS–soy pulp composites.

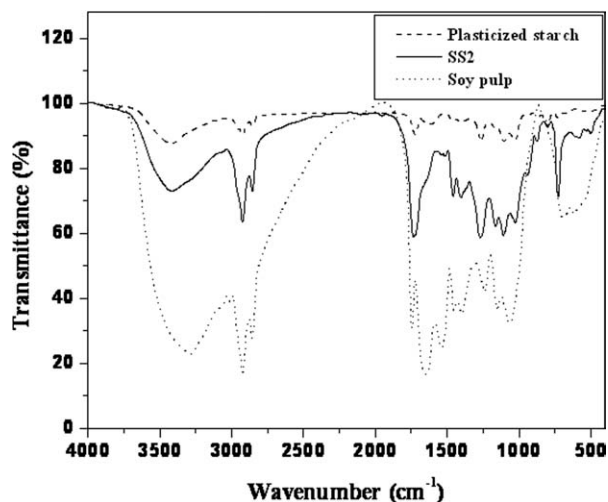


Figure 2. FTIR spectra for TPS, soy pulp, and SS2 composite.

the blends. As a result, the blended products show enhanced mechanical properties. The composites exhibited brittle properties when the amount of soy pulp exceeds 10 wt % resulting in catastrophic decrease of the tensile strength and modulus values of SS composites. The decreasing of tensile modulus with increase in soy pulp content (>10 wt %) was due to conglomeration of soy pulp inside the matrix.<sup>15</sup> Higher elongation at break (EB) value of the composites indicates higher ductility of the material and lower EB indicates lower ductility of materials. In case of SS0, the EB value is highest and monotonically decreased with increment in filler content explaining increasing brittleness among SS composites.

Smaller particle size of soy filler provides higher stiffness. The enhancement in flexural strength of SS composites obtained might be due to presence of the soy filler which helped to transfer the stress from TPS to soy filler. With increasing filler content from 0 to 10 wt %, flexural strength and modulus of SS composites increased 98% and 41%, respectively (Table II). But further

increment in filler content, both strength and modulus decreased drastically due to heterogeneous mixing of filler particles in starch matrix by reducing interaction between them.<sup>16</sup> SS2 (containing 10 wt % filler) composite showed highest mechanical strength, hence it was considered as optimum composite.

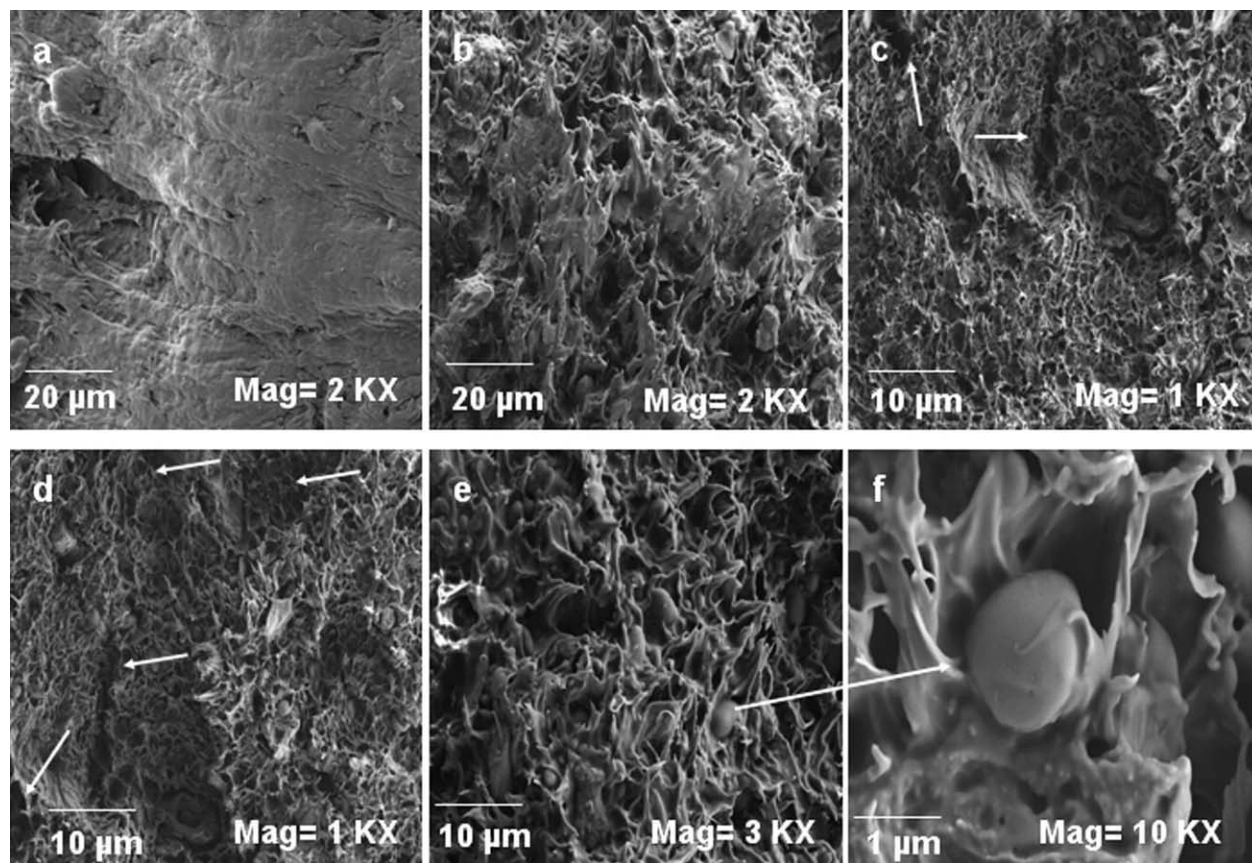
#### FTIR Analysis of Soy Pulp, Starch, and SS Composite

FTIR spectroscopy was used to examine the chemical interactions between soy pulp and starch in SS composite. The infrared spectra of soy pulp, TPS, and optimized SS pulp composite (SS2) are presented in Figure 2. In the spectrum for starch film, the broad band obtained at around  $3422\text{ cm}^{-1}$  is for  $\text{—OH}$  stretching of free, inter- and intramolecular hydrogen bonded hydroxyl groups. The peaks at  $2921\text{ cm}^{-1}$  and  $1463\text{ cm}^{-1}$  correspond to the  $\text{C—H}$  ( $\text{—CH}_3$ ) stretching and bending, respectively, while the band at  $1625\text{ cm}^{-1}$  is assigned to the  $\text{—OH}$  bending of water. The peak appeared at around  $1724\text{ cm}^{-1}$  is for  $\text{—C=O}$  bond stretching of ester groups present in TPS (Ma et al.<sup>17</sup>). Similarly, soy pulp shows a broad peak at  $3286\text{ cm}^{-1}$  for  $\text{—NH}$  and  $\text{—OH}$  stretching, while other two important peaks at around  $2925\text{ cm}^{-1}$ ,  $1744\text{ cm}^{-1}$  correspond to  $\text{—CH}$ , and  $\text{—C=O}$  stretching, respectively.<sup>18</sup> When two polymers are compatible in a physical blend (or composite), a distinct interaction in the form of hydrogen-bonding or dipolar interaction between the chains of filler and those of polymer matrix are reflected by shifting in characteristic IR peak position.<sup>19</sup> Such shifting of peaks occurred in case of SS2 composite towards higher/lower wavenumbers than those of starch and soy pulp. The  $\text{—OH}$  stretching peak of SS2 composite in the FTIR spectrum was found at a lower frequency, i.e., at around  $3418\text{ cm}^{-1}$  than that of TPS. This might be due to the formation of new hydrogen bonds between hydroxyl group of soy pulp and that of starch during composite fabrication. The hydroxyl groups that participated in the hydrogen bonding within starch molecules were destroyed by combined thermal and mechanical effect during composite fabrication (extrusion). New hydrogen bonds between the reactive hydroxyl groups in TPS molecules and the active groups (soy proteins) in soy pulp were hence formed.<sup>20</sup> Since the interaction between hydroxyl groups of filler and matrix is strong,

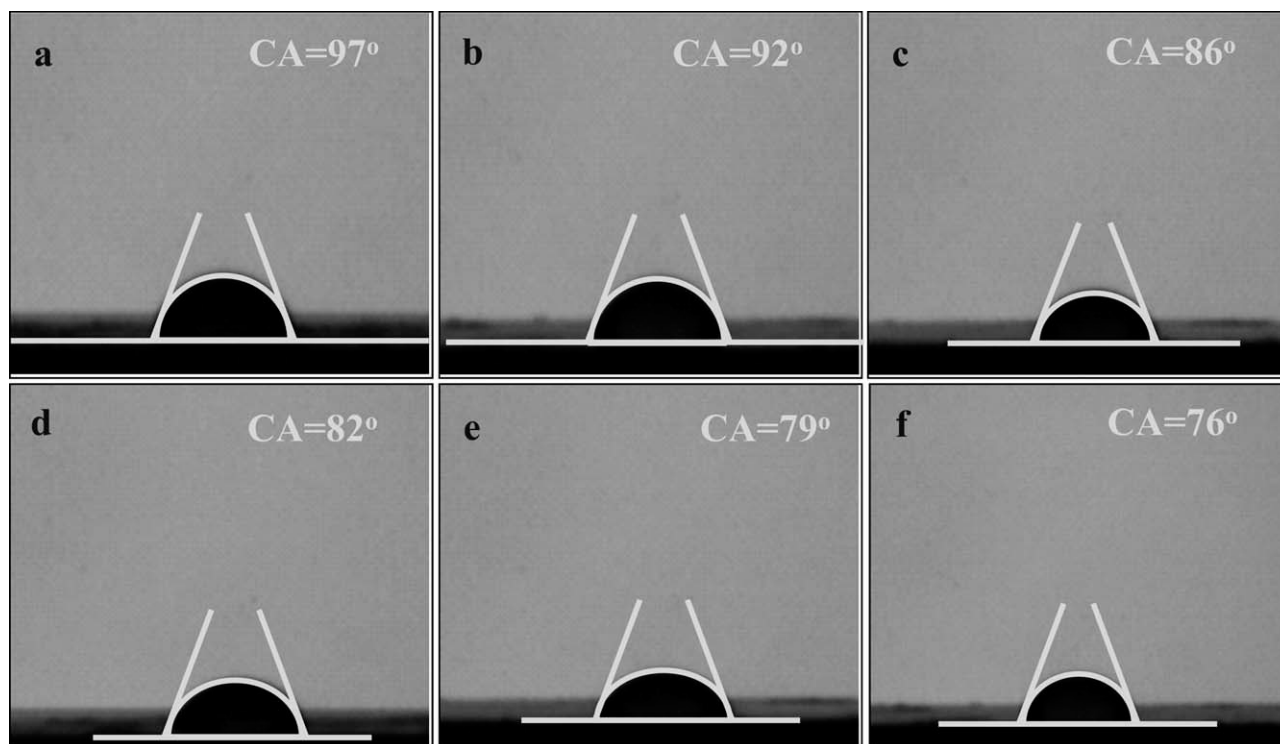
Table III. Peak Assignment in the FTIR Spectra for Plasticized Starch, Soy Pulp, and SS2 Composite

Peak assignment	Frequency ( $\text{cm}^{-1}$ )		
	Soy pulp	Plasticized starch	SS2 composite
$\text{—OH}$ (st) (hydrogen bonded)	3286	3422	3418
$\text{—NH}$ (st) (in secondary amide)	3429	-	3422
$\text{—CH}_3$ (asym) (st), $\text{—CH}_2$ (sym) (st)	2925, 2858	2921, 2858	2924, 2856
$\text{—C—O}$ (st) (in ester)	1744	1724	1734
$\text{—OH}$ (b)	1616	1625	1632
$\text{—C—N}$ (st) (in secondary amide)	1538	-	1515
$\text{—CH}_3$ (b) and $\text{—CH}_2$ (b)	1452, 1406	1463, 1400	1459, 1403
$\text{—C—N}$ (st) (in tertiary amide)	1239	-	1269
$\text{—C—O}$ (st) in $\text{C—O—H}$	1153	1104	1163
$\text{—C—O}$ (st) in $\text{C—O—C}$	1064	1026	1028
$\text{—C—O}$ (b) in $\text{C—O—C}$	693	730	726

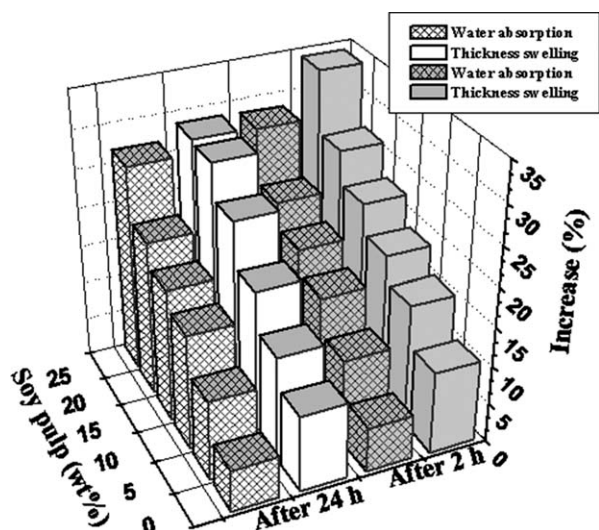
t, stretching; b, bending; asym, asymmetric; sym, symmetric.



**Figure 3.** SEM photographs of (a) TPS (smooth surface), (b) SS2, (c) SS2 (fractured portions are marked by arrow), (d) SS5 (fractured portions are marked by arrow), (e) SS2 (surface at higher magnification), and (f) Completely matrix coated soy pulp granule.



**Figure 4.** CA photographs of (a) SS0, (b) SS1, (c) SS2, (d) SS3, (e) SS4, and (f) SS5.

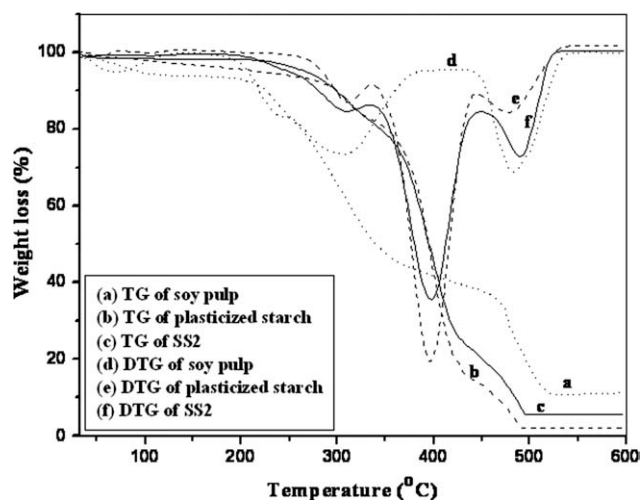


**Figure 5.** Water absorption and thickness swelling of TPS-soy pulp composites after 24 h in distilled water and 2 h in boiling water.

the peak for  $\text{—OH}$  shifts towards higher frequency than that of filler. A close examination revealed significant differences in intensity and position of peaks and wavenumbers for starch, soy pulp, and composite indicating some chemical interaction between filler and matrix. Other peaks in the FTIR spectrum assigned to different functional groups are presented in Table III.

#### FE-SEM Analysis of Tensile-Fractured Composite

FE-SEM micrographs of matrix (TPS) and tensile fractured surfaces of the SS2 and SS5 (10 and 25 wt % of soy pulp loaded) composites are shown in Figure 3. Highly moisture sensitive soy pulp filler was reinforced in smooth surface of TPS [Figure 3(a)] and produced strong SS composite [Figure 3(b)]. The surface morphological difference in the form of roughness and cracks between 10 wt % (mechanically optimized) filler loaded composite (SS2) and 25 wt % filler (high amount) loaded composites (SS5) are presented in



**Figure 6.** TG/DTG curves for TPS, soy pulp, and SS2 composite.

Figure 3(c,d). A number of cavities in the form of cracks were found on SS5 composite surface as compared to that of SS2, due to higher filler loading [Figure 3(d)]. In SS2 composite [Figure 3(e)], a few filler particles were found on the matrix surface at higher magnification. These fillers were homogeneously separated within the matrix with complete coating [Figure 3(f)] and are responsible for improvement in mechanical properties. On the other hand, for SS5 composite [Figure 3(d)], higher loading of filler material makes agglomerated structure. This weakened the bonding between filler and matrix and hence affected the mechanical properties adversely.

#### CA and Water Sorption of SS Composites

Water sensitivity is an important criterion for many practical ecofriendly applications of SS products. The photographs of SS composites taken during CA measurement with CA value are shown in Figure 4. The higher the CA value of a material, the lower will be its hydrophilic property.<sup>21</sup> For SS0 (TPS), CA value is maximum ( $97^\circ$ ) and it decreased with increase in soy

**Table IV.** Thermal Decomposition of Plasticized Starch, Soy Pulp, and SS2 Composite

Specimens	Degradation temperature ( $^\circ\text{C}$ )			Mass loss during degradation (%)			Degraded component
	Start	Mid	End	Start	Mid	End	
TPS	45	52	70	0.5	1.0	1.4	Trapped moisture
	273	310	338	7.2	10.7	18.0	Polyhydroxylic groups
	345	397	444	19.2	55.5	86.1	Decomposition of starch
	455	481	534	87.8	94.4	97.7	Carbon residue
Soy pulp	45	70	120	1.3	3.2	5.9	Moisture and protein
	200	226	250	7.3	10.3	17.5	Hemicellulose
	270	309	374	23.1	38.3	56.1	Cellulose
	447	483	537	61.5	75.1	89.1	Carbon residue
SS composite (SS2)	48	51	62	1.2	1.3	1.4	Trapped moisture
	269	312	333	5.3	13.2	17.9	Polyhydroxylic groups
	352	398	436	21.2	51.3	77.1	Cellulose
	455	494	521	81.4	94.4	94.6	Carbon residue

pulp amount. This consequence explains high water absorption property of SS composites with higher filler content, and adhesion between filler and matrix. It was found after both the experiments, the thickness swelling value of SS composites increased with increase in soy pulp loading. The water absorption and thickness swelling percentages of SS composites are presented in Figure 5. Because of the presence of polyester, the water sorption by SS0 was found only 5.8 and 6.1%, after immersing in distilled water at RT for 24 h and diffusing in boiling water 2 h, respectively. With increasing filler content, the water sorption value of SS composite increased under both the experimental conditions. This is due to the presence of soy pulp, which is composed of hydrophilic polymeric material (soy protein) containing hydroxyl groups (Table I) responsible for more water absorption.<sup>22</sup> Thickness swelling of SS composites can be affected by several factors such as compatibility between filler and matrix, matrix loading. SS5 exhibited thickness swelling of 28.6% after its immersion in distilled water for 24 h. It also showed highest thickness swelling of 30.2% after immersion in boiling water for 2 h due to poor interaction between starch and soy pulp. It also displayed maximum water absorption of 25.4% in boiling condition for 2 h. The increase in water absorption might be due to increased number of microvoids caused by the larger amount of poor bonded area between the filler and the matrix polymer.<sup>23</sup> Since these composites showed good response towards water sorption, it is expected that the developed composites can be biodegradable in compost condition after their use. Hence, developed composites are ecofriendly and sustainable in nature unlike plastic.

#### Thermal Properties of Composites

Thermogravimetric analysis (TGA) was performed for soy pulp, TPS and optimized SS2 composites, where the mass loss due to the volatilization of the degradation products was monitored as a function of temperature. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of above samples are presented in Figure 6. Thermal degradation temperature with percentage of mass loss and degraded components are given in Table IV. The initial DTG peak obtained at around 100°C for TPS and SS2 composite due to the evaporation of trapped moisture. Soy pulp showed a broader moisture elimination peak in the range between 45 and 120°C as compared to other two samples due to the moisture evaporation along with protein degradation as reported.<sup>24</sup> For soy pulp, one shoulder peak at 226°C and second peak at 309°C were obtained for degradation of hemicellulose and  $\alpha$ -cellulose present in pulp respectively. Similarly for TPS first degradation peak obtained at 310°C corresponded to decomposition of polyhydroxylic groups and second degradation peak at 397°C is for high molecular weight groups present in starch. The SS2 composite exhibited two thermal degradation peaks at 312°C due to the elimination of polyhydroxylic groups and at 398°C for decomposition of cellulose. For all three samples, a degradation peak at around 480–495°C was obtained for carbon burning as reported.<sup>25</sup> So, the developed SS composite (with 10 wt % filler content) was thermally stable up to 312°C, which is slightly better than the thermal stability of TPS (310°C).

#### CONCLUSIONS

The purpose of this study was to develop biocomposites of TPS using soy pulp as a biofiller. The composites developed with 10

wt % loading of soy filler showed 112% and 98% increase in tensile strength and flexural strength, respectively, due to better interaction between matrix and filler in form of hydrogen bonding confirmed by FTIR analysis. With an increase in filler loading, enhanced water sorption of the composites might have facilitated faster biodegradation. Thermal analysis of the composites revealed that filler has little contribution towards improving the thermal stability of composite.

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