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# Simultaneous plasticization and blending of isolate soy protein with poly(butylene succinate – co – adipate)

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**ABSTRACT:** Agrarian proteins, due to their good film forming properties, moderate cost, and biodegradable nature, have been extensively studied to develop affordable packaging materials. However, when compared to conventional polymers, isolated proteins based polymers have poor mechanical and barrier properties. Blending with others polymers seems to be a viable option to overcome these issues. The present work focuses on the preparation of isolated soy protein (ISP) / poly[(butylene succinate)-co-adipate] (PBSA) blends with different ratios by extrusion and injection moulding using glycerol and water mixture as plasticizer. PBSA is bio-based, biodegradable, and its relatively low melting point is compatible with the processing temperature of ISP. Two different processing strategies were used and compared for the preparation of blends. In the novel single step approach, ISP, plasticizers (glycerol and water) and PBSA are dry mixed and extruded all together in a co-rotating twin-screw extruder. In the regular two-step approach, plasticized protein is prepared by extrusion of ISP with a glycerol/water mixture, followed by a second extrusion step of plasticized protein with PBSA. Prepared blends were characterized for their morphology, thermal, dynamic mechanical and mechanical properties. The mechanical properties of the blends prepared by single step process are roughly similar to those produced by two-step process; this indicates the efficiency of one-step melt processing of PBSA with isolated soy protein involving plasticization, denaturation, melt-melt mixing and morphology development in the extruder, this compounding method being more-over less time consuming.

## 1 INTRODUCTION

Petroleum-derived plastics have been widely used for packaging materials. However, these are non-degradable and causes serious ecological issues [1,2]. In recent years, the use of isolated soy protein (ISP) from biomass has been reported for packaging applications [3,4], due to its biodegradability, low cost and easily available in nature. ISP is one of the most important green polymers used today to produce biodegradable materials to reduce the dependence and consumption of petroleum based plastics [5]. However, green polymers prepared from unmodified isolated soy protein (ISP) are highly hydrophilic, which results in poor mechanical properties [6]. Many efforts have been made to improve its processability, flexibility and moisture resistance by modifying it with different plasticizers and/or blending it with other biodegradable polymers [7,8]. Poly [(butylene succinate)-co-adipate] (PBSA) is an eco-friendly polyester which has attracted much attention due to its biodegradability, relatively low melting point (100°C), exactly matching the processing temperature of ISP [9].

In that context, the present study aims at developing plasticized ISP/PBSA blends prepared by melt-blending. Up to now, most of the isolated soya protein-based blends have been prepared by using two-step processes [10] where ISP is firstly plasticized using suitable plasticizers, and then, plasticized ISP was mixed with other polymers. This process is time consuming and costly. Therefore, in the present study, a single step compounding approach will be adopted, ISP, plasticizers (glycerol

and water), sodium sulphite (SS) and PBSA being dry-mixed and all together extruded in a co-rotating twin-screw extruder. Prepared blends will be characterized for their morphology, thermal, dynamic mechanical and mechanical properties. For the purpose of comparison, blends will also be prepared by the conventional two-step method.

## 2 EXPERIMENTAL

### 2.1 Materials

Isolated soy protein (ISP) (PROFAM 974, ADM foods, Breda, The Netherlands) with 90% of protein on a dry basis was the basic material of the present study. ISP has 6% of original moisture, 4% of fat and 5% of ash (based on supplier data). ISP was stored at 23°C with 50% relative humidity (RH), to avoid the fluctuations in moisture content.

Analytical grade glycerol (Sigma-Aldrich, Saint Louis, USA) was used as plasticizer in combination with water. Usage of sodium sulfite (SS) (Prolabo, France) avoided the cross-linking of proteins. The auxiliary bio-based polymer was PBSA (PBE 001, Natureplast, France). PBSA granules were dried in a vacuum oven for 12h at 60°C before the extrusion process.

### 2.2 Processing conditions

ISP, glycerol and SS were premixed in the ratio 49, 40 and 1wt.% respectively, along with 10wt. % of water for 10 min in a kitchen mixer. This mixture was stored for 12h at 23°C with

50% relative humidity (RH). Then, in one-step process (hereafter called as “method-1”) the above-mentioned mixture (i.e. ISP+Glycerol+SS+water) was melt blended at different ratio of PBSA (75, 50 and 25wt. %) at 130-135-140°C in a co-rotating twin-screw extruder (Haake Rheomex PTW 16 OS, Thermo Scientific, Germany) at 75 rpm. The residence time of extrusion process was about 2 min. In the two-step processing technique (hereafter called as “method-2”) the following procedure was adopted. Firstly, the mixture of 49 wt.% ISP + 40 wt.% glycerol, 1 wt.% SS and 10 wt.% water was extruded to obtain plasticized soy protein (PISP) granules. Then, PISP granules were melt blended with various weight percentages of PBSA granules by extrusion (Haake Rheomex PTW 16 OS, Thermo Scientific, Germany). Blends compositions adopted for the study are summarized in Table 1. Finally, extruded PBSA, PISP and blend granules were injection-moulded (Babyplast 6/10P, Cronoplast, Italy) into standard test specimen for tensile and dynamic mechanical analysis. During injection moulding, the temperature profile ranged from 135 to 137°C, flow rate was 1.5 cm<sup>3</sup> s<sup>-1</sup>, holding pressure 25 bars, and cooling time was 30s at a 60°C mould temperature. In case of neat PBSA, the temperature profile was set at 114-116°C with a 50°C mould temperature whereas other moulding parameters were the same as for blends. Before testing, all samples were stored in controlled humidity chamber for one week at 23°C with a controlled relative humidity (RH) of 53%.

Table 1. Composition of PISP/PBSA blends and processing parameters.

Method	Extrusion temperature (°C)	Sample code	Content (wt.%)	
			PBSA	PISP
1	130 – 135	M1 75/25	75	25
	130 – 135	M1 50/50	50	50
	135 – 140	M1 25/75	25	75
2	130 – 135	M2 75/25	75	25
	130 – 135	M2 50/50	50	50
	130 – 138	M2 25/75	25	75

### 2.3 Morphology characterization (SEM)

The morphology of the PISP/PBSA blends was studied using a tabletop SEM (Neoscope JCM 6000, Jeol instrument, USA) under high vacuum, operating at 5kV using cryo-fractured injection-moulded samples previously coated with a thin gold layer using gold sputter coater (Polaron 20mV).

### 2.4 Thermal behaviour

The thermal stability of the produced materials was assessed by thermo-gravimetric analysis (TGA/DSC1, Mettler Toledo, Switzerland). Samples masses ranging from 3 to 5 mg were heated from 25°C to 600°C at a rate of 10°C/min under nitrogen atmosphere.

Thermal transitions of PISP/PBSA blends were determined by using differential scanning calorimetry (DSC 8500, Perkin

Elmer, USA). The tests were performed under nitrogen. The sample was sealed in an aluminium pan and heated from -60°C to 200°C at a heating rate of 10°C/min and then cooled. The samples were subsequently heated again from -60°C to 200°C. The melting temperature ( $T_m$ ), the crystallization temperature ( $T_c$ ) and melting enthalpy ( $\Delta H_m$ ) were determined from the respective endotherms and exotherms. The degree of crystallinity ( $X_c$ ) was calculated from their corresponding melting enthalpy according to the equation 1.

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} * 100 \quad (1)$$

where  $\Delta H_m$  is the melting enthalpy of PISP/PBSA;  $\Delta H_m^0$  is the melting enthalpy for 100% crystalline PBSA and was taken as 110.8 J/g. [11]

### 2.5 Tensile testing

The mechanical properties of injection-moulded blends were studied by using a tensile machine (Lloyd LRK Instruments, Ametek, USA) following the ISO 527-1 standard. The pre-load force was fixed at 0.5 N and the crosshead speed was 1mm/min for the determination of tensile strength, elongation and the Young’s modulus. Five samples of each composition were tested and the average values reported.

### 2.6. Dynamic mechanical analysis (DMA)

The dynamic mechanical properties of the produced blends were determined using a dynamic mechanical analyzer (DMA+150, Metravi B, France) at a frequency of 1 Hz. The displacement amplitude was 3.5µm. The samples were heated from -60°C to 100°C at a heating rate of 2°C/min and the flow rate of nitrogen was 10 mL/min. DMA specimens (4 mm ×10 mm ×15 mm) were cut from injection-moulded impact bar samples. Two specimens of each composition were tested. The storage modulus ( $E'$ ) and the loss factor ( $\tan \delta$ ) were recorded as a function of temperature.

## 3 RESULTS AND DISCUSSION

### 3.1 Phase Morphology

Figure 1 presents the morphology of the different samples observed by scanning electron microscopy.

Unprocessed original ISP appears as solid particles (Figure 1a). During the processing of ISP, in the presence of a plasticizer (glycerol and water), ellipsoidal ISP particles are transformed into a homogeneous matrix (Figure 1b). Plasticizers penetrate into ISP granules and destroy the inner hydrogen bonds, and presence of sodium sulphite eliminates protein–protein interactions and promotes the protein–plasticizer interactions. [12,13] The plasticized mouldable thermoplastic material, called plasticized isolated soy protein (PISP), is homogeneous as no ISP particles are visible.

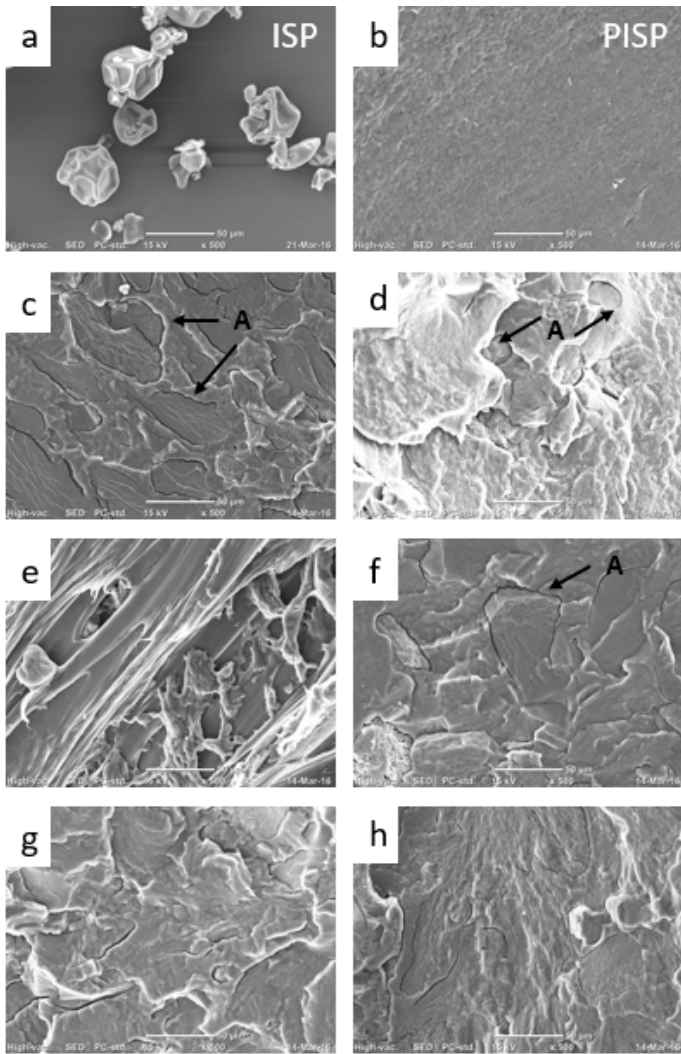


Figure 1. SEM image of ISP particles (a) and cryogenic fractured of PISP (b) and PBSA/PISP blends: (c) M1 75/25, (d) M2 75/25, (e) M1 50/50, (f) M2 50/50, (g) M1 25/75, (h) M2 25/75.

From Figure 1c, it is clear that plasticized isolated soy protein in “M1 75/25” presents an ordered network structure, while in “M2 75/25” no network is visible and PISP appears as dispersed phase with weaker interface (Figure 1d – where weaker interface is marked as “A”). In both methods, PISP appears as network structure with PBSA as dispersed phase with larger blocks. The Figure 1e further demonstrates the tightly bound interface between PBSA and PISP with network structure indicating a better interfacial adhesion compared to that of Figure 1f. Eventually in M2 50/50, the low interfacial adhesion between the two phases leads to severely coarsened phase structures for both domains. But, at higher PISP content weaker interface is observed for M1 25/75 (Figure 1g) and a better interface between the PBSA and PISP is observed in two-step processing method (Figure 1h). Overall morphological observation reveals that PISP/PBSA blend morphology depends not only on the phase volume fraction, but also on the processing method [14].

### 3.2 Thermo gravimetric Analysis (TGA)

When temperature increases, PBSA shows one degradation weight loss step whereas PISP shows two prominent weight losses. The first weight loss corresponds to the elimination of water, the second weight loss in the range 150-350°C decom-

poses into two under parts. The first one is plasticizer degradation and the second one is protein degradation. Three-step weight loss was observed in PBSA/PISP blends (Figure 2). The first weight loss below  $\sim 110^{\circ}\text{C}$  is due to evaporation of moisture. The weight loss in the range of 250-380°C is ascribed to the plasticizer evaporation and the final weight loss beyond 380°C is due to decomposition of protein bonds and PBSA molecules degradation. Thermal stability of PBSA/PISP is reduced with increasing PBSA content due to immiscibility between PBSA and PISP. However, the processing method has no effect on the thermal stability of PBSA/PISP blends, as there is only a little difference of TGA records between method-1 and method-2.

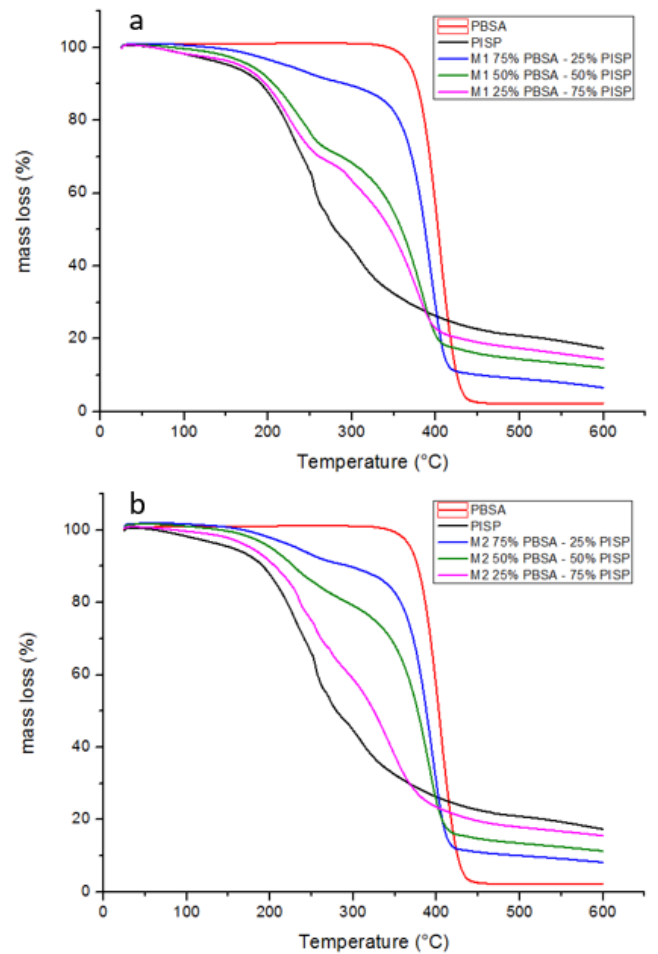


Figure 2. Thermo gravimetric analysis of melt processed PBSA, PISP and PBSA/PISP blends (a) Method-1 and (b) Method-2.

### 3.3 Differential Scanning Calorimetry (DSC)

Thermal transitions and crystallinity degrees of PISP/PBSA blends prepared via method-1 and method-2 are summarized in Table 2. DSC data of PISP was discarded due to the lack of endothermic and exothermic peaks. Whatever the compounding method is, the percentage of crystallinity ( $X_c$ ) and melting temperature ( $T_m$ ) of blends are lower than those of neat PBSA. However, the  $X_c$  and  $T_m$  are almost similar for both the processes except for the blend with 75/25 composition; the crystallinity degree of M2 75/25 blend is 38% while that of M1 75/25 is 30%. In this latter case, higher reduction in  $X_c$  indicates that, PISP hampers the crystallization of PBSA much more.

Sample	T <sub>c</sub> (°C)	T <sub>m</sub> (°C)	X <sub>c</sub> (%)
PBSA	37.8	89.2	41
M1 75/25	38.8	87.8	30
M1 50/50	34.6	86.9	32
M1 25/75	36.9	86.5	19
M2 75/25	33.7	85.8	38
M2 50/50	34.7	83.0	31
M2 25/75	35.9	86.5	18

Table 2. DSC data of PISP, PBSA and PISP/PBSA blends.

### 3.4. Dynamic Mechanical Analysis

The storage modulus and  $\tan \delta$  of PBSA, PISP and PBSA/PISP blends prepared via method-1 and method-2 are shown as a function of temperature in Figure 3. The blending of PISP with PBSA using both methods leads to a slight increase of storage modulus ( $E'$ ) for PBSA/PISP (75:25) in both glassy and rubbery regions (up to ambient temperature) and it falls at a level between PISP and PBSA for PISP/PBSA (50:50) blends. But, PISP/PBSA (75:25) blends show marginally higher modulus than PISP only at ambient temperature (Figure 3a and c) in both methods. However, method-1 materials show marginally higher storage modulus values than those prepared by method-2. The increase in initial storage modulus may also be a result of the intermolecular interactions between carboxyl group of PBSA and hydroxyl, amide and carboxyl group of PISP.

Considering  $\tan \delta$ , PISP obviously has two main relaxation peaks. The peak at around 60 °C is assigned to the glass transition relaxation ( $\alpha$ -relaxation) of the isolated soy protein, and the other peak at around -50 °C is attributed to the  $\beta$ -transition of the soy protein [15]. The  $\tan \delta$  peak of PBSA is observed at -30°C. In case of M1 75/25 and M2 75/25, only one peak corresponding to T<sub>g</sub> of PBSA is observed at -30°C and the relaxation peaks of PISP does not appear. Similarly, in M1 25/75 and M2 25/75, only one relaxation peak corresponding to  $\beta$ -transition is observed at -50°C. This is due to the dominance of glycerol rich phase during dynamic mechanical analysis. But, M1 50/50 and M2 50/50 blends show notable difference from other blends (Figure 3 b and d). In the case of M2 50/50 blends, two relaxation peaks corresponding to  $\beta$ -transition of glycerol rich phase and T<sub>g</sub> of PBSA appear; this could mean that M2 50/50 is heterogeneous. In these cases, the lower transition temperature of PBSA shifts slightly to lower temperature revealing that the molecular structures of glycerol rich isolated soy protein were disturbed by the segments of the polyester during blending process when blended with PBSA in equal composition.

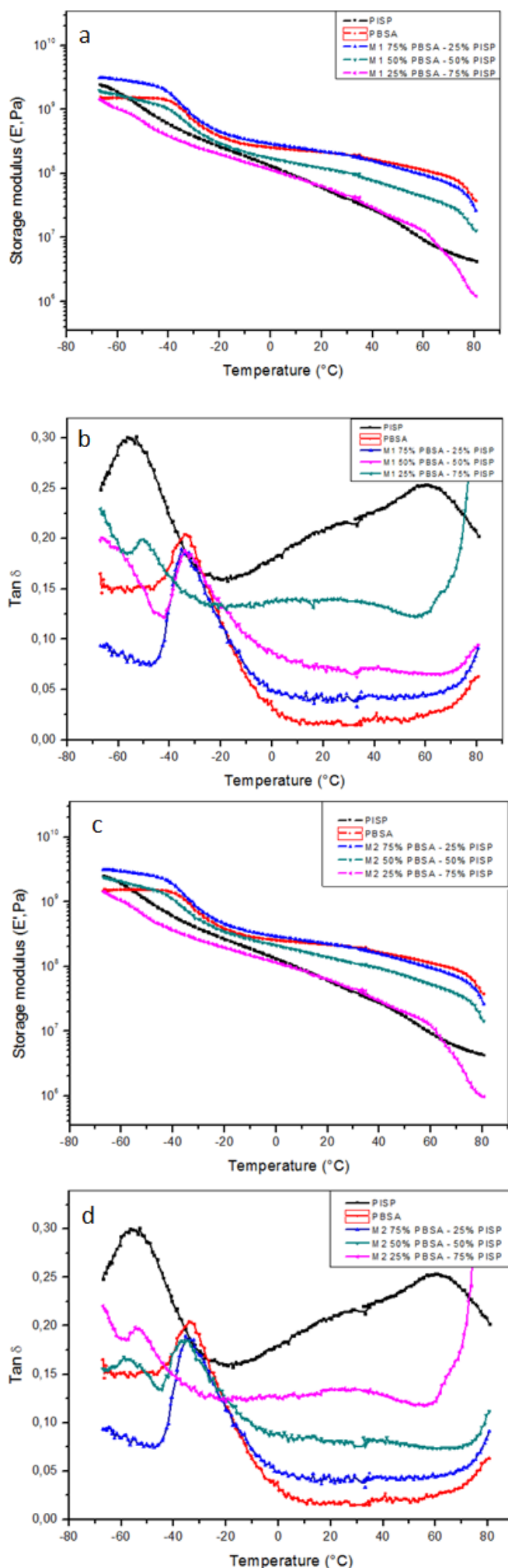


Figure 3 Storage modulus (a and c) and loss factor  $\tan \delta$  (b and d) for Method-1 (a and b) and for Method-2 (c and d).



### 3.5. Mechanical properties

Table 3 summarizes the tensile properties of PISP, PBSA and PISP/PBSA blends prepared by the two different methods. The tensile strength, Young's modulus and elongation at break increase with increasing PBSA content (Table 3). Comparing both the processing methods, the tensile strength is almost similar, whereas the Young's modulus is moderately higher for method-2 and elongation at break slightly higher for method-1. This is due to the fact that blends compounded with method-1 resulted in interconnected phase structure with increased intermolecular interaction between PBSA and PISP. But in case of method-2, the two-step processing resulted in slight cross-linking of isolated proteins and presence of PISP as blocks in PBSA might have restricted the movement of PBSA chains and thus decreased the elongation at break. These results are consistent with the previous observations of the phase morphologies of these two blend-systems, where method-1 blends demonstrated a much finer co-continuous phase structure than method-2 blends.

Sample	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
PBSA	26±1.3	256±6	266±10
PISP	1.6±0.2	30±1	21±4.4
M1 75/25	14.3±0.2	171±13	87±18
M1 50/50	6.4±0.2	117±2	27±3
M1 25/75	2.7±0.2	69±3	10±1
M2 75/25	14±0.3	189±8	76±7
M2 50/50	7.7±0.3	126±7	20±2
M2 25/75	3.2±0.1	76±3	10±1

Table 3. Tensile properties of PBSA/PISP blends.

### CONCLUSION

PISP/ PBSA blends were successfully prepared by melt mixing with different compositions via single-step and two-step compounding methods. PISP/PBSA blend morphology depends not only on the phase volume fraction, but also on the processing method. Blends prepared by one-step method show an interconnected network structure of PISP particles with homogeneous phase structure. In case of two-step method, PISP appears as droplets with weak interface in PISP/PBSA blends. The one-step method therefore enables thorough mixing and thus better dispersion of PISP into the PBSA. The thermal stability of blends decreases with increasing PISP content due to poor interaction between PISP and PBSA, but with only little deviation between both processing methods. Similar tensile strengths are also observed, whereas the newly developed one-step method leads to a moderately lower Young's modulus (- 11%) and a slightly higher elongation at break. Overall results indicated that, properties of the single-step processed blends are roughly similar to those of the two-step process. As consequence, this study suggests that simultaneous plasticization and blending of isolated soy protein with PBSA in one-step extrusion process can be a cost effective and less time consuming method to prepare PISP/ PBSA blends.

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