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A new approach for morphology control of poly(butylene adipate-*co*-terephthalate) and soy protein blends

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ABSTRACT

In contrast to most studies in the literature where soy protein was used as a particulate filler in hydrophobic thermoplastic polymers, in this study, soy protein concentrate (SPC) was processed as a plastic to blend with poly(butylene adipate-*co*-terephthalate) (PBAT). By adjusting water content in the formulated SPC from low to high prior to compounding, SPC exhibited behaviors ranging from rigid filler to deformable filler to plastic during blending. Detailed phase morphology of the blends was revealed by transmission electron microscopy and field emission scanning electron microscopy. Evidences showed that SPC formed percolated thread structures when additional water was added to SPC prior to compounding. Study of dynamic rheology also confirmed the formation of interconnected network structure. Accordingly, tensile mechanical properties were greatly improved for those blends with percolated SPC thread structures. The molecular weight change of PBAT in blends and influence of processing on soy protein solubility were also examined.

1. Introduction

Many studies have demonstrated that soy protein (SP) is a promising alternative to petroleum-based plastic materials. In the presence of water, SP can undergo gelation with heating and is subsequently plasticized by the water present, displaying plastic characteristics under shearing. The processibility and processing methods of SP plastics, however, strongly depend on the water content in SP. Compression molding of SP requires only a small amount of water. For example, Paetau et al. showed that soy protein isolate (SPI) with 7.1% water and soy protein concentrate (SPC) with 5% water could be compression molded [1]. Sun et al. also compression molded the 7S-riched and 11S-riched SP containing 10% extra water into uniform plastics [2]. Such compression molded SP demonstrated fairly high tensile strength (~40 MPa) and modulus (~1.6 GPa) but could not be reshaped by melt processing. Chen and Zhang also prepared SPI sheets with varying levels of glycerol by compression molding and demonstrated similar tensile properties [3]. With higher levels of water present, SP can be processed by extrusion or injection molding. Zhang et al. melt compounded SPI in the presence of sufficient water (e.g. 60 parts per 100 parts of SPI) and/or glycerol by extrusion with temperature varying between 60 and 115 °C from the feed section to die, and subsequently extruded the compounded SP pellets (retaining ca. 25% water) into smooth sheets with the die temperature varying between 100 and 120 °C, depending on the formulations [4]. The extruded SPI sheets similarly displayed high yield strength up to 40 MPa. Recently Ralston and Osswald studied the viscosity of SPI/corn-starch blends compounded with 19% glycerol, 1% soy oil and 30% water [5]. The blends with water content adjusted to 10% showed comparable viscosities to LDPE in the temperature range of 180–230 °C. These studies demonstrated the plastic nature of soy protein due to the fact that SP gelates in the presence of certain levels of water and is subsequently plasticized. Nevertheless, the plastics based on SP alone or SP blended with other natural polymers are highly water/moisture sensitive and brittle with moisture loss. To overcome these shortcomings, blending SP with biodegradable hydrophobic polymers has received extensive study. So far most studies have merely used SP as particulate organic filler to mix with other polymers, e.g. poly(butylene succinate-*co*-adipate) [6], polycaprolactone [6–8], poly(hydroxyl ester ether) [9] and poly(butylene adipate-*co*-terephthalate) [10]. Although these blends generally showed greater water resistance, processability, and/or toughness than neat SP plastics, they often exhibited lower strength than both neat SP plastics and polymers. We previously studied the blends of poly(lactic acid) (PLA) with SPI or SPC formulated with extra water [11]. Co-continuous structure and percolated thread structure were noted for the compounded SPC/PLA blends and SPI/PLA blends, respectively,

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Table 1
Solubility of SPC isolated from different blends.

Reagent(s)				% Protein dissolved[a]			
	Urea	Na_2SO_3	Acrylonitrile	Unprocessed SPC	PBAT/SPC-H_2O[c]	PBAT/n-SPC[d]	PBAT/dry-SPC[e]
Buffer I				34.4 (0.71)[b]	1.3 (0.03)	0.65(0.01)	1.97 (0.04)
Buffer II	X			40.0 (0.83)	7.0 (0.15)	2.6 (0.05)	4.91 (0.10)
Buffer III	X	X	X	48.4 (1.00)	18.4 (0.38)	9.1(0.19)	13.0 (0.27)

[a] % Protein dissolved was calculated on the basis of the total SPC sample weight.
[b] Values in parentheses were normalized with respect to the solubility of the unprocessed SPC in buffer III.
[c] The blend was prepared from SPC containing 22.5% H_2O.
[d] The blend was prepared from native SPC (containing 7.5% H_2O).
[e] The blend was prepared from dry SPC (containing 0.6% H_2O).

suggesting that SP behaved like a melt in blending. These blends demonstrated significantly higher tensile strength and modulus than those with SP as filler. Similarly, Sailaja et al. recently studied polypropylene blends with soy flour containing 33% glycerol and 19% water, and the resulting blends exhibited greater tensile strength than the blends from dry soy flour [12]. However, the phase morphology of the blends was not elucidated in that study. Since in the presence of water and/or other plasticizers SP behaves like a melt under shear and water plays a determining role in its flowability, it is important to know the influence of water content in SP on the morphology and properties of the resulting blends.

In this study, PBAT/SPC blends were prepared by extrusion compounding and the test specimens of the resulting blends were prepared by injection molding. The effects of water content on the development of SPC phase morphology were examined in detail. Rheological and tensile properties of the blends were studied. The effects of water content in SPC on the changes of soy protein molecular structure and molecular weight of PBAT were also examined. The main objective of this study was to utilize the melt character of SP for flexible design of the morphological structure of the blends, hence manipulate their properties. To the best of our knowledge, the effect of processing SP as a plastic component on morphological structure of the blends has not been reported elsewhere.

2. Experimental

2.1. Materials

SPC (Arcon F) was provided by ADM (Decatur, IL), and contained ca. 7.5 wt% moisture as received. PBAT (Ecoflex F BX 407) was provided by BASF (Florham Park, NJ), having a weight-average molecular weight of 71.7 kDa and a polydispersity of 1.60. Maleic anhydride (MA) (95%) was purchased from Aldrich. MA grafted PBAT (MA-*g*-PBAT) was prepared by reactive extrusion using dicumyl peroxide 98% as initiator, and the residual MA was removed under high vacuum at 80 °C [13]. The degree of grafting was 1.40 wt% as determined by titration method.

2.2. Preparations of blends and test specimens

SPC was formulated and contained the following ingredients: SPC (100 parts, on the basis of dry weight), sodium sulfite (0.5 parts), glycerol (10 parts) and/or water. Six levels of water content in the formulated SPC were selected: 0.6 (from vacuum drying at 70 °C for 12 h), 7.5 (native, as received), 10, 12.5, 17.5 and 22.5 wt%, respectively. The water content at the levels higher than that of native SPC was achieved by the addition of extra water. The formulated SPC was mixed using a kitchen blender, then stored in sealed plastic bags and left overnight at room temperature to equilibrate. The mixture of the formulated SPC (hereafter “pre-compounding SPC”, 30 parts on the basis of dry SPC weight), PBAT (67 parts) and MA-*g*-PBAT (3 parts) was compounded using a co-rotating twin-screw extruder (Leistriz ZSE-18) equipped with 18 mm screws having an *L*/*D* ratio of 40. The screw speed was maintained at 80 rpm for all runs, and the eight controlled temperature zones from the first heating zone to the die adaptor were set to 99, 110, 145, 145, 145, 145, 145, and 140 °C, respectively. The vents of the extruder were closed, and the screws had dynamic seal elements near the inlet to minimize the escape of water vapor. The residence time was ca. 2 min during extrusion compounding. The extrudate was cooled in a water bath and subsequently granulated by a strand pelletizer. Pellets were exposed in the air for 4 h to further evaporate the residual surface moisture and then dried in a convection oven at 90 °C for more than 12 h (the residual moisture was less than 1%). Test specimens were prepared by a Sumitomo injection molding machine (SE 50D) with barrel zone temperatures set to 155, 160, 160 and 155 °C from the feeding section to the nozzle. Mold temperature was set to 50 °C and cooling time was ca. 30 s. All samples were conditioned for one week at 23 ± 2 °C and $50 \pm 5\%$ RH prior to mechanical test and characterization.

2.3. Tensile and rheology tests

Dynamic rheological properties were measured using a strain-controlled rheometer (Rheometric Scientific, RDA III) with a parallel-plate geometry ($d = 25$ mm). The gap distance between the parallel plates was 1 mm for all tests. A strain sweep test was initially conducted to determine the linear viscoelastic region of the materials, then a dynamic frequency sweep test (strain: 3%, frequency: 0.01–500 rad/s) was performed at 160 °C. All test samples were cut from the injection molded specimens after conditioning. Since the moisture content of the specimen after conditioning was found to be ca. 1%, no additional protection during the test was taken.

Tensile tests were performed on a screw-driven universal testing machine (Instron 4466) equipped with a 10-kN electronic load cell and machine grips. The testing was conducted at a cross-head speed of 5 mm/min with strain measured using a 25-mm

Table 2
GPC results of PBAT molecular weight change after processing.

Sample	Unprocessed PBAT	Molded PBAT	PBAT/SPC-H_2O[a]	PBAT/n-SPC[b]	PBAT/dry-SPC[c]
M_w (Da)	71,700	71,800	64,600	60,200	65,400
M_n (Da)	44,900	44,200	40,600	36,800	40,800
M_w/M_n	1.60	1.62	1.59	1.63	1.60

[a] The blend was prepared from SPC containing 22.5% H_2O.
[b] The blend was prepared from native SPC (containing 7.5% H_2O).
[c] The blend was compounded from dry SPC (containing 0.6% H_2O).

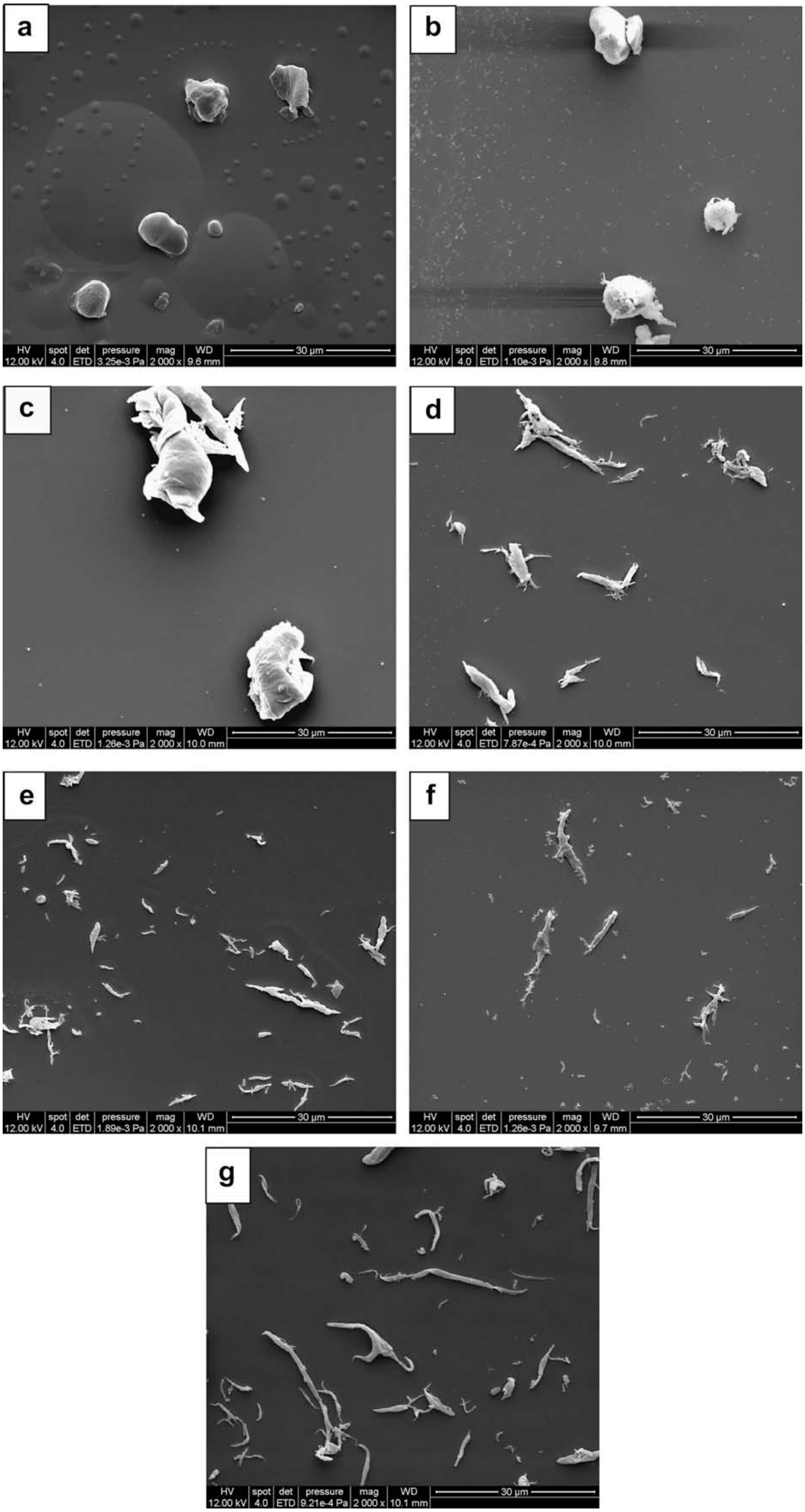

Fig. 1. FE SEM micrographs showing the influence of water content in the pre-compounding SPC on the deformation of the SPC phase. SPC was isolated by Soxhlet extraction of the PBAT matrix. a, Unprocessed SPC; b, SPC-0.6% H_2O; c, SPC-7.5% H_2O; d, SPC-10% H_2O; e, SPC-12.5% H_2O; f, SPC-17.5% H_2O; g, SPC-22.5% H_2O.

extensometer (MTS 634.12E-24). All tests were carried out according to the ASTM standard and 5 replicates were tested for each sample to obtain an average value.

2.4. Microscopy

Transmission electron microscopy (TEM, Jeol 1200 EX, accelerating voltage 100 kV) was used to give the high resolution phase morphology of the blends. TEM ultrathin sections from the injection molded samples were prepared using an ultramicrotome (Powertome X, Boeckeler Instrument) at −80 °C under a liquid nitrogen environment. Field emission scanning electron microscopy (FE SEM, Quanta 200F) was applied to investigate the microstructure of the SPC domains. The PBAT phase was removed by Soxhlet extraction using $CHCl_3$, and the sample was wrapped in a filter paper pouch to minimize the disturbance of the SPC phase by the solvent flow. The isolated SPC was gently suspended in $CHCl_3$ and spin coated onto mica slices at the low speed limit. The unprocessed SPC particles were also suspended in $CHCl_3$ and spin coated in the same way. All FE SEM specimens were sputter coated with gold prior to examination.

2.5. Solubility test of soy protein

The SPC samples used for protein solubility test were performed as follows. A piece of the molded sample (ca. 5 g) was added to 50 mL $CHCl_3$ to dissolve the PBAT component, followed by filtration. The residue on the filter paper was treated with the same procedure for 3 more times to assure the complete removal of PBAT. The unprocessed native SPC was treated with the same extraction procedure and used as a control. The combined filtrate was added to acetone to precipitate the PBAT which was used for molecular weight analysis. Solubility tests of the above SPC samples were performed in three buffer solutions [14]: buffer I contained 0.0182 M $NaHCO_3$ and 0.0318 M Na_2CO_3 and had a pH value of 10; buffer II was obtained by adjusting buffer I to contain 8 M urea; buffer III was obtained by adjusting buffer II to have 0.1 M Na_2SO_3 and 0.1 M acrylonitrile. The dissolution of the SPC sample was carried out as follows [14]. 10 mL buffer solution and 0.1 g SPC sample were added to a small capped bottle and stirred using a magnetic bar for 60 min. The solution was centrifuged at 5000 g for 5 min, and the supernatant was removed for protein analysis using Bradford assay.

2.6. Gel permeation chromatography (GPC)

PBAT molecular weight before and after processing was analyzed by a Viscotek's Complete Triple Detector Platform and GPCmax™ front-end chromatography setup. The Triple Detector Platform was composed of light scattering, refractive index, and viscometer. The samples (∼4.0 mg/mL) were injected twice at a volume of 100 μL and eluted at 45 °C in HFIP (0.02 M KTFA) at 1.0 mL/min flow rate for best signal quality. Two ViscoGEL I-series columns (2× I-MBHMW) were required to achieve the desired results.

3. Results and discussion

3.1. Changes in soy protein solubility and PBAT molecular weight

It is understood that thermoplastic extrusion of SP results in formations of not only new disulfide bonds [15,16] but also peptide bonds [17] between SP molecules. Our previous study also showed that the extruded SPI sheet swelled greatly in water but retained its integral shape, suggesting that SP formed a network structure after processing [4]. In this study, the change of SP molecular structure after processing was examined by solubility test [14]. Table 1 gives the results of solubility in different buffers of the unprocessed SPC and SPC isolated from three representative blends. Buffer I only dissolved protein molecules without strong

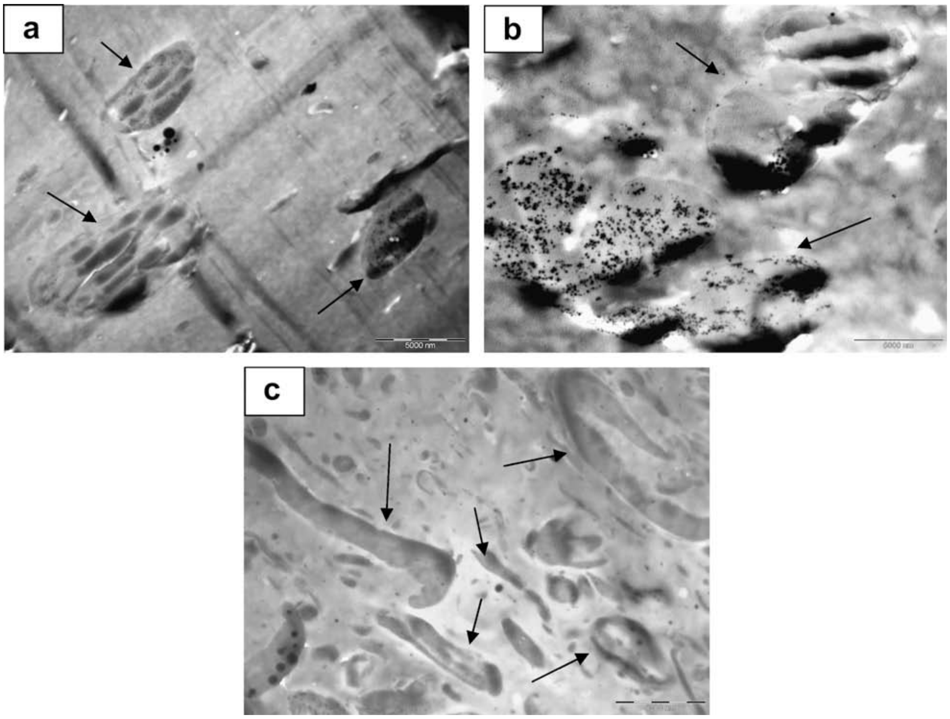

Fig. 2. TEM micrographs of the PBAT/SPC (70/30 w/w) blends. The scale bar is 5000 nm. (a) SPC-0.6%H_2O; (b) SPC-7.5%H_2O; (c) SPC-22.5%H_2O.

intra- and intermolecular bonding; buffer II containing urea would, in addition, dissolve small aggregates caused by non-covalent forces. Because sodium sulfite can cleave disulfide bridges that cause large aggregates of protein, buffer III could dissolve proteins cross-linked by disulfide bonds [18]. Acrylonitrile in buffer III could cyanoethylate the resulting sulfhydryl groups to prevent them from reoxidizing. If the total protein content of SPC is 70 wt% (per specification of the product), the results indicate that buffer III only dissolved ca. 70% proteins in the unprocessed native SPC. It should be mentioned that this result was lower compared to the reported solubility (ca. 94%) of proteins from the native SPC using the same buffer and dissolution procedure [14]. Nevertheless, since all SPC samples were subjected to the same dissolution testing, it is still valid to use the solubility results for a qualitative evaluation of the effect of processing conditions on SP molecular structure changes. For this purpose, all other solubility values were normalized with respect to that of the unprocessed SPC in Buffer III. The results indicate that melt blending process led to a drastic decrease of SP solubility in all buffers, suggesting that a significant amount of protein molecules were converted into insoluble supramolecules. It is noted that water content in the pre-compounding SPC also played an important role in the solubility of SP after blending. The decrease in solubility was the least for the SPC with 22.5% H_2O and the most for the native SPC (containing 7.5% H_2O), while the solubility of dry SPC (containing 0.6% H_2O) fell in the middle. However, no further investigation of the mechanism of molecular changes was attempted in this study. The extensive crosslinking and/or agglomeration of SP molecules would make the SPC phase behave like a solid in the matrix in the subsequent melt process of the blends, as elucidated later in the discussion of dynamic rheological results.

The possible degradation of PBAT after processing was also examined. In Table 2, the molecular weight of neat PBAT showed almost no change after experiencing the same processes as the blends, suggesting a good thermal stability of neat PBAT in processing. However, the molecular weight of PBAT suffered ca. 9, 10 and 16% loss in the blends with 0.6, 22.5 and 7.5% H_2O in the pre-compounding SPC, respectively. The molecular weight decrease of PBAT in the blends could be attributed to both hydrolysis and thermal degradation during compounding. Considering that the dried SPC still contained ca. 0.6% residual moisture, the copolyester PBAT likely underwent hydrolysis in the processing conditions. Furthermore, the various functional groups of SP such as carboxyl and amino groups might also accelerate the hydrolysis and thermal degradation of PBAT. Nevertheless, no further investigation was attempted in this study to detail the mechanism of PBAT degradation in the compounding process.

3.2. SPC phase structure

In order to better understand the influence of water on the mixing behavior of SPC and its phase structure, the PBAT matrix was removed by Soxhlet extraction and then the isolated SPC phase was examined by FE SEM (Fig. 1). For better observation, the samples were prepared by spin coating the suspension of the

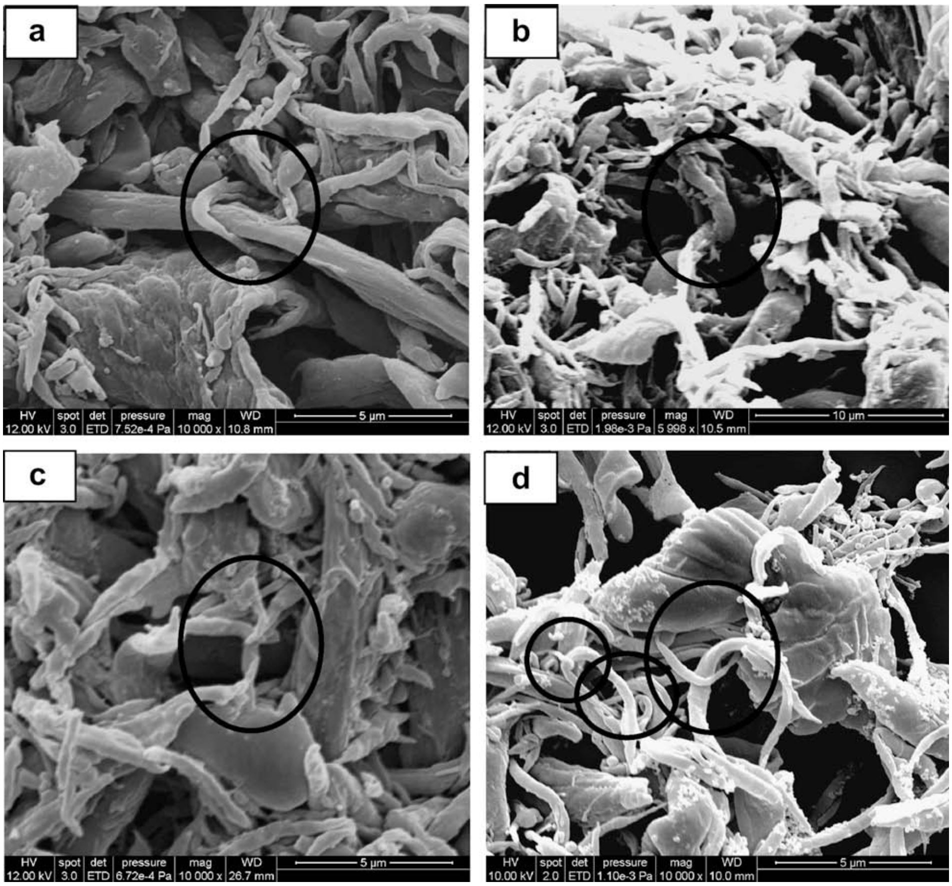

Fig. 3. FE SEM micrographs of microstructure of the SPC domains in the PBAT/SPC (70/30 w/w) blends after the removal of PBAT by Soxhlet extraction. a, SPC-10%H_2O; b, SPC-12.5%H_2O; c, SPC-17.5%H_2O; d, SPC-22.5%H_2O.

isolated SPC in $CHCl_3$ on mica slices. The unprocessed SPC appeared like ordinary particulate particles (Fig. 1a). In contrast, SPC in the blends clearly experienced morphological change, depending on the water content in the pre-compounding SPC. Dry SPC largely retained the sizes and shapes of the unprocessed SPC (Fig. 1b), suggesting it behaved like a rigid particulate filler in mixing with the matrix. When native SPC (containing 7.5% H_2O) was used, the SPC phase appeared ellipsoidal and its average domain size was apparently larger when compared with dry SPC in the blend (Fig. 1c). With an extra amount of water added to native SPC, however, SPC appeared as fine threads (Fig. 1d–g). These results suggest that water content in the pre-compounding SPC played a critical role in the development of the SPC phase structure in the blends. SP particles were likely hardened by heat in the mixing process [19], so dry SPC was dispersed like a rigid particulate filler in the matrix without clear deformation and size change. The larger domain sizes of SPC for the blend from native SPC was probably due to its 7.5% moisture as received. It is well-recognized that the main mechanism governing the morphology development of blend is the balance between droplet breakup and coalescence [20]. During compounding the dispersed phase is subjected to deformation under shear force, stretched to threads and broken into small droplets [21]; vice versa the droplets can coalesce. The size and shape changes of the SPC phase in the blend prepared from native SPC may suggest that the 7.5% water in native SPC could gelate the SPC to a certain degree and make the neighboring particles fused together but was not sufficient to render the gelated SPC high enough deformability. Therefore, the SPC phase was not able to experience a significant deformation and breakup. With a certain amount of extra water, SPC could be better plasticized and possess appropriate deformability under the specific compounding conditions. However, the viscosity of the SPC phase was still anticipated to be fairly high due to the high molecular interactions and the extensive aggregation and crosslinking of SP during processing as indicated by the above solubility analysis. Therefore, SPC coalescence surpassed its breakup during processing, and SPC melt was stretched along the shear direction and extended to threads.

Fig. 2 shows the TEM micrographs of the blends prepared from SPC with three representative levels of water content. When dry, native, and SPC containing 22.5% H_2O were used, the SPC phase in the resulting blends appeared as ordinary particulates, enlarged ellipsoids, and fine threads, respectively. These results were in good agreement with the results from the above FE SEM analysis. The TEM analysis of phase morphology of the blends further confirmed that with increasing water content in the pre-compounding SPC, the SPC phase experienced changes from rigid particles to deformable fillers to plastic.

PBAT had a density of ca. 1.27 g/cm^3. If the density of the SPC phase was assumed to be ca. 1.35 g/cm^3 according to Jong's previous study [22], the volume fraction of the SPC phase was approximately 28.7 vol% for the PBAT/SPC (70/30 w/w) blends. According to Isichenko's study [23], for filler with an aspect ratio of 1, its percolation threshold is at ca. 29 vol%. Therefore, it is reasonable to consider that the dispersed SPC threads, which should have aspect ratios significantly larger than 1, had higher probability to form 3-D interconnected networks in respective blends [24]. In fact, the formation of the percolated SPC thread network structure could be observed directly from the remains after removal of the PBAT matrix by Soxhlet extraction (Fig. 3). The interconnection and even some interlocking loops of the SPC threads were clearly noted in the blends prepared from SPC containing 10–22.5% H_2O. This percolated SPC thread network structure drastically changed the melt rheological behavior and mechanical properties of the blends, as discussed in the following sections.

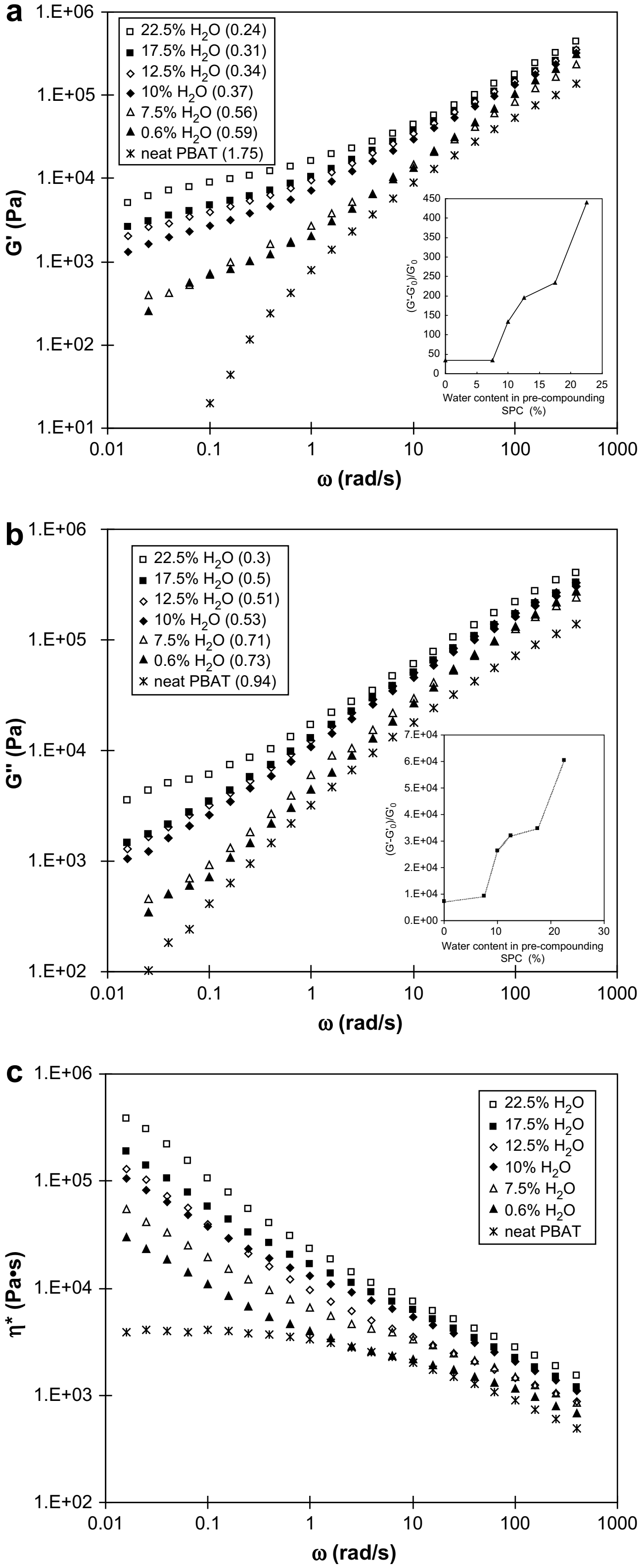

Fig. 4. Effect of water content in the pre-compounding SPC on the dynamic rheological properties of the PBAT/SPC (70/30 w/w) blends. Strain = 3%, temperature = 160 °C. The insets showed the increase in relative moduli with respect to those of the neat PBAT (G'_0 and G''_0) at $\omega = 0.01$ rad/s as a function of water content in pre-compounding SPC. The values in parentheses were the slopes of $\log(G')$ or $\log(G'')$ vs. $\log(\omega)$ in the terminal zone.

3.3. Rheological properties and percolation

In an earlier study, we demonstrated that the SPI sheet containing 10% glycerol displayed an elastic modulus of 1.23 GPa [4], which is ca. 12 times the modulus of PBAT. The SPC phase in the present blends could also be anticipated to have an elastic modulus of the similar level. Furthermore, due to its extensive agglomeration and crosslinking as well as drying of most residual moisture after blending, the SPC phase in the blends could not be melted again in the subsequent processing. Therefore, these blends with SPC thread structures became *in-situ* formed composites. Dynamic rheological properties are very sensitive to structure and interactions within the polymer melt. Since the solid structure of a material can be preserved under small-strain test conditions, dynamic rheology testing is often used for the evaluation of morphological structure of polymer blends and composites [25,26]. In the terminal (low frequency) zone, the PBAT melt demonstrated a typical liquid-like behavior – logarithmic storage (G') or loss (G'') modulus vs. logarithmic angular frequency (ω) showed a smooth linear relationship by $G' \propto \omega^{1.75}$ and $G'' \propto \omega^{0.94}$, respectively (Fig. 4). The blends with 30% SPC not only exhibited much higher G', G'' and complex viscosity (η^*) values than PBAT, but also demonstrated drastically different terminal behaviors. Irrespective of frequency, both G' and G'' increased monotonically with increasing water content in the pre-compounding SPC. The viscoelastic response of the blends was mainly altered at low frequencies, where G' and G'' exhibited weak frequency dependences [27]. With 22.5% H_2O in the pre-compounding SPC, the slope of log(G') vs. log(ω) of the resulting blend was 0.24, indicating a significant pseudo-solid-like behavior of the melt. This result suggests that an interconnected network structure of anisometric filler – a characteristic solid or gel-like structure had formed in the system [28]. The effect of water content in the pre-compounding SPC can be also seen from the insets of Fig. 4a and b, where the relative increase in G' and G'' with respect to the neat polymer became phenomenal at 10% H_2O, suggesting the critical water content for the percolation threshold. On the other hand, in the terminal zone the plots of log(η^*) vs. log(ω) changed from a Newtonian (primary) plateau (Fig. 4c) for the neat PBAT to a clear shear-thinning behavior for the blends, providing more evidence of elastic behavior due to the solid network structure of SPC. Fig. 5 shows the changes of the log G' and G'' with water content in the pre-compounding SPC [29]. Clearly, G' and G'' were very sensitive to the formation of SPC percolation at which log G' and log G'' exhibited drastic increases. Again, the result suggests that the critical water content for percolation threshold was at 10%.

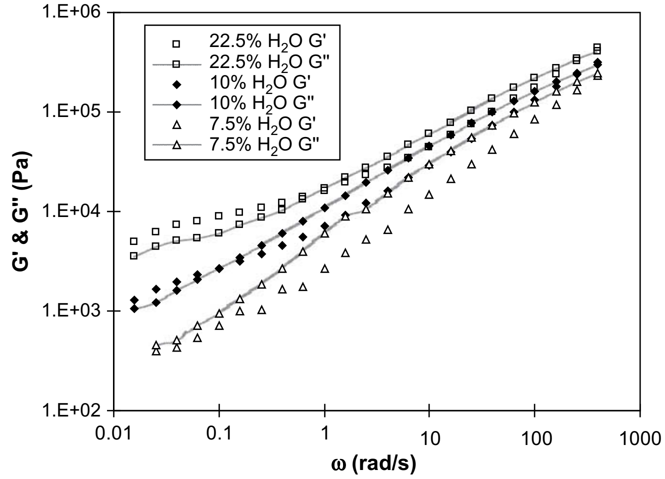

Fig. 6. Log G' and log G'' vs. log ω curves for the PBAT/SPC (70/30 w/w) blends prepared from SPC containing 22.5%, 10% and 7.5% H_2O.

Further evidence of the formation of a pseudo-solid-like network of percolated threads is also noted in Fig. 6, where variations of G' and G'' of the blends vs. ω are compared. The PBAT/SPC-7.5% H_2O blend, in which SPC was dispersed as particles, displayed a lower G' than G'' over the whole frequency range. However, with the buildup of network structure, in the terminal zone G' exceeded G'' due to the pseudo-solid like behavior. At higher frequencies, crossover of G' and G'' was noted and it was probably due to the destruction of the network structure at high shear rates. Similar crossover was also reported for the polystyrene/carbon nanotube composites with percolated structures [29]. Expectedly, the crossover of G' and G'' was observed for all those PBAT/SPC blends prepared from the SPC containing 10–22.5% H_2O. It is worth mentioning that the crossover point shifted to higher frequency with water content in the pre-compounding SPC. The frequencies at which the crossover occurred were 0.1, 0.25, 0.4 and 1 rad/s for the PBAT/SPC blends prepared from SPC containing 10, 12.5, 17.5 and 22.5% H_2O, respectively.

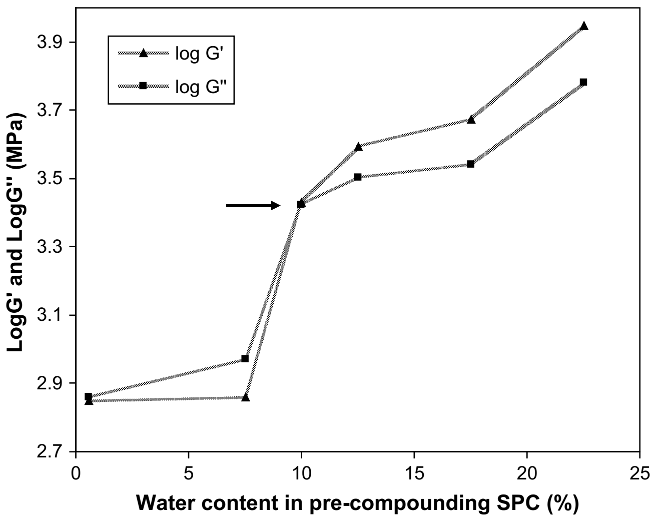

Fig. 5. Log G' and log G'' as a function of water content in the pre-compounding SPC. The rheological data were obtained from Fig. 4a and b at the frequency of 0.1 rad/s.

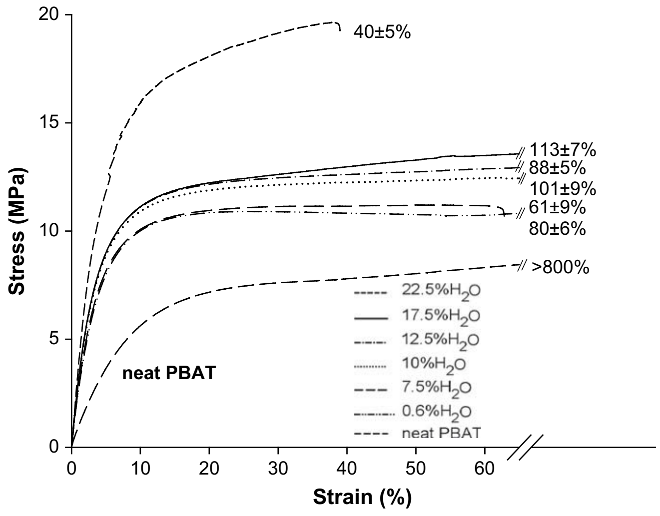

Fig. 7. Stress–strain curves of PBAT/SPC (70/30 w/w) blends from SPC formulated with different levels of water.

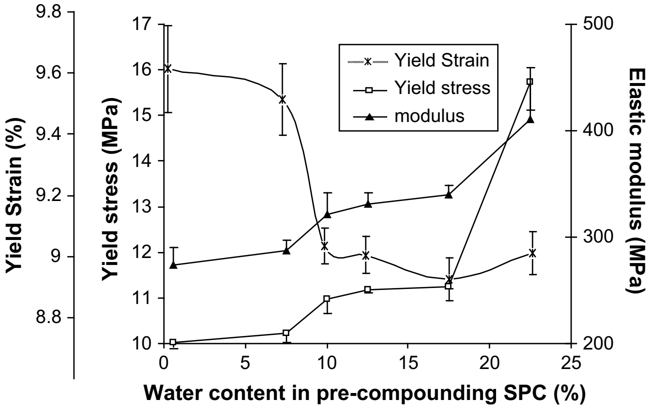

Fig. 8. Effect of water content in the pre-compounding SPC on yield stress/strain and modulus of PBAT/SPC (70/30 w/w) blends.

3.4. Tensile mechanical properties

Fig. 7 shows the tensile stress–strain curves of neat PBAT and the blends. PBAT behaved like a very soft polymer, displaying low yield stress, modulus, and high ductility (not broken within the tester frame used). The blends displayed a typical tensile behavior for a system consisting of a rigid phase dispersed in a soft matrix. All blends showed higher stresses and moduli than that of neat PBAT, but exhibited great reduction in elongations. The large increases in yield strength and modulus were direct consequences of the suppression of the global cooperative chain movement of PBAT by the percolated SPC network structure. It is noted that reinforcing effect increased with water content in the pre-compounding SPC, while elongation decreased. Though SPC only existed as particulate fillers in the PBAT/SPC-0.6% H_2O (dry) and PBAT/SPC-7.5% H_2O (native) blends, with a loading level of 30% it still exerted a significant restriction to the chain movement of PBAT, resulting in great increases in yield stress and modulus and decrease in elongation. Nevertheless, all blends still showed fairly good ductility. The influences of water content in the pre-compounding SPC on yield stress and modulus of the blends are further compared in Fig. 8. Apparently, when additional water was added to the native SPC, the yield stress and modulus of the resulting blend began increased dramatically. This phenomenon indicated the interconnected network structure of threaded SPC started to form at ca. 10% H_2O in the pre-compounding SPC. Accordingly, the elongation at break also took a large reduction with the formation of SPC network structure. The mechanical properties were in good agreement with the variation in morphological structure of the blends observed in electron microscopy and rheology tests.

4. Conclusions

The phase morphology of PBAT/SPC (70/30 w/w) blends with PBAT can be manipulated greatly by exploring the plastic characteristics of SPC. By varying water content in the pre-compounding SPC from low to high, the SPC phase changed from rigid filler to deformable filler to plastic in the compounding process. While dry SPC behaved like a rigid filler in blending, native SPC (containing 7.5% H_2O) could fuse with each other and showed a very limited deformability in the process, resulting in the formation of large domain sizes. When containing additional water, SPC began to behave like a plastic and underwent considerable deformation during mixing with PBAT. Specifically, with 10% or more H_2O in the pre-compounding SPC, SPC existed as threads in the resulting blends which showed a clear tendency to form an interconnected network structure of SPC. Rheological study and tensile tests further indicated that the critical water content in the pre-compounding SPC for percolated SPC thread structure is ca. 10%. The molecular weight of PBAT in blends exhibited a 9–16% decrease depending on the pre-compounding SPC condition, suggesting that water present in blending process and the functional groups in SP both influenced the hydrolysis and thermal degradation. Melt processing greatly reduced the solubility of soy protein, suggesting that extensive aggregation and crosslinking occurred during blending.

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References

[1] Paetau I, Chen C, Jane J. Ind Eng Chem Res 1994;33(7):1821–7.
[2] Sun XS, Kim H, Mo X. J Am Oil Chem Soc 1999;76(1):117–23.
[3] Chen P, Zhang L. Macromol Biosci 2005;5(3):237–45.
[4] Zhang J, Mungara P, Jane J. Polymer 2001;42(6):2569–78.
[5] Ralston BE, Osswald TA. J Polym Environ 2008;16(3):169–76.
[6] John J, Bhattacharya M. Polym Int 1999;48(11):1165–72.
[7] Zhong Z, Sun XS. Polymer 2001;42(16):6961–9.
[8] Mungara P, Zhang J, Zhang S, Jane J. In: Gennadios A, editor. Protein-based films and coatings. CRC Press; 2002. p. 621–38.
[9] Wang C, Carriere CJ, Willett JL. J Polym Sci Part B Polym Phys 2002;40(19): 2324–32.
[10] Graiver D, Waikul LH, Berger C, Narayan R. J Appl Polym Sci 2004;92(5): 3231–9.
[11] Zhang J, Jiang L, Zhu L, Jane J, Mungara P. Biomacromolecules 2006;7(5): 1551–61.
[12] Sailaja RRN, Girija BG, Madras G, Balasubramanian N. J Mater Sci 2008;43(1):64–74.
[13] Jiang L, Huang J, Qian J, Chen F, Zhang J, Wolcott M, et al. J Polym Environ 2008;16(2):83–93.
[14] Hager DF. J Agric Food Chem 1984;32(2):293–6.
[15] Jenkins SL. US Patent 3496858; 1970.
[16] Cumming DB, Stanley DW, de Man JM. J Food Sci 1973;38(2):320–3.
[17] Burgess LD, Stanley DW. Can Inst Food Sci Technol Aliment 1976;9(4):228–31.
[18] Abtahi S, Aminlari M. J Agric Food Chem 1997;45(9):4768–72.
[19] Jong LJ. Appl Polym Sci 2005;98(1):353–61.
[20] Thomas S, Groeninckx G. Polymer 1999;40(21):5799–819.
[21] Sundararaj U, Macosko CW. Macromolecules 1995;28(8):2647–57.
[22] Jong L. Composites Part A 2006;37:438–66.
[23] Isichenko MB. Rev Mod Phys 1992;64(4):961–1043.
[24] Willemse R, Posthuma A, Van Dam J, Gotsis A. Polymer 1999;40(4):827–34.
[25] Utracki LA. Polymer alloys & blends. New York: Carl Hanser; 1989. p. 131–74.
[26] Du M, Zheng Q, Yang H. Nihon Reoroji Gakkaishi 2003;31(5):305–11.
[27] Romeo G, Filippone G, Fernandez-Nieves A, Russo P, Acierno D. Rheol Acta 2008;47(9):989–97.
[28] Utracki LA. Rheology and processing of multiphase systems, vol. II. New York: Carl Hanser; 1987. p. 7–59.
[29] Kota A, Cipriano B, Duesterberg M, Gershon A, Powell D, Raghavan S, et al. Macromolecules 2007;40(20):7400–6.