**Enhancing distributive mixing of immiscible polyethylene/thermoplastic starch blend
through zeolite ZSM-5 compounding sequence**

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ABSTRACT

The aim of this work was to explore the effect of zeolite ZSM-5 (ZSM5) incorporation sequence on the phase morphology, microstructure, and performance of polyethylene/thermoplastic starch (PE/TPS) films. Two processing sequences were used for preparing PE/TPS/ZSM5 composites at a weight ratio of PE to TPS of 70:30 and ZSM5 concentrations of 1–5 wt%: (i) melt compounding of PE with ZSM5 prior to melt blending with TPS (SI); and (ii) TPS was compounded with ZSM5 prior to blending with PE (SII). Distributive mixing and mechanical properties of PE/TPS blend were greatly enhanced when ZSM5 was incorporated via SII. These were caused by both the higher affinity between PE and ZSM5, compared to that of TPS and ZSM5, and the reduction of TPS viscosity after compounding with ZSM5, leading to migration of ZSM5 from TPS dispersed phase toward PE matrix and increase in breakup of TPS droplets during SII sequence.

Keywords: Polyethylene; Thermoplastic starch; Zeolite; Blending sequence; Distributive mixing; Viscosity

1. Introduction

Polyethylene (PE) film is commonly used in flexible packaging applications for food and nonfood products due to its superior mechanical and moisture barrier properties. As the demand for PE continues to increase, a large volume of plastic waste is generated due to its improper disposal. To alleviate this problem, there has been an increasing interest in reducing the use of

PE by blending it with biodegradable and compostable thermoplastic starch (TPS). Unfortunately, these two materials are immiscible due to the difference in their chemical nature and polarity, and their blends exhibit poor mechanical properties. Several strategies have been investigated to overcome this drawback such as using chemically modified starch (Kiatkamjornwong, Thakeow, & Sonsuk, 2001), and PE (Wang, Yu, & Yu, 2005), adding chemical compatibilizers (Cercle, Sarazin, & Favis, 2013), or incorporating nano/micro inorganic fillers into the PE/TPS blend (Thipmanee & Sane, 2012). To improve the compatibility between PE and TPS, maleic anhydride and maleic anhydride-graft-copolymer are often employed through reactive compatibilization and used as chemical compatibilizer, respectively (Cercle et al., 2013; and Wang et al., 2005). However, these methods are less desirable for applications especially when associated with safety and health concerns (Harrats, Fayt, & Jérôme, 2002). Alternatively, incorporating nontoxic inorganic fillers, which is more economical and technically simpler, could be adopted to improve the mixing of PE/TPS blend. Previous studies have demonstrated that incorporation of carbon black (Wu, Li, & Jiang, 2010), nanosilica (Elias, Fenouillot, Majeste, & Cassagnau, 2007 and Jarnthong, Nakason, Lopattananon, & Peng, 2012), organoclays (Sinha Ray & Bousmina, 2005), or zeolites (Djoumaliisky & Zipper, 2004 and Thipmanee & Sane, 2012) was capable of improving the mixing of immiscible and partially miscible blends. However, both the chemical affinity between filler and polymer, as well as the mixing sequence, could play important roles in determining the distribution of the blend components, as well as microstructure, and properties of ternary composites (Elias et al., 2007; Jarnthong et al., 2012; and Pastor et al., 2012).

Elias et al. (2007) and Jarnthong et al. (2012) reported that the distributions of hydrophilic silica nanoparticles in polypropylene/polystyrene (PP/PS) and epoxidized natural

rubber/polypropylene (ENR/PP) blends, respectively, were determined by the affinity between silica nanoparticles and blend components as well as the mixing sequence. When silica nanoparticles were pre-mixed with a lower affinity polymer (i.e., PP) prior to blending with the more favorable polymer (ENR and PS), the majority of silica particles migrated toward the higher affinity component. On the contrary, when silica nanoparticles were pre-mixed with the more favorable polymer prior to blending with the less affinity polymer, most of the nanoparticles were still confined in the higher affinity polymer. Furthermore, incorporation of silica nanoparticles reduced the size of the ENR and PS dispersed phases because the presence of silica nanoparticles restricted the coalescence of dispersed domains.

Zeolites, nanoporous crystalline aluminosilicate materials with pore sizes ranging from 3 to 15 Å, have also been used as a filler to improve the physical and mechanical properties of neat polymers (e.g., PE and PLA) (Biswas et al., 2004 and Yuzay, Auras, Soto-Valdez, & Selke, 2010) and polymer blends (e.g., recycled PE/PP/PS) (Djournaliisky & Zipper, 2004). Djournaliisky and Zipper (2004) have reported on the ability of activated natural zeolite to improve mixing of recycled PE/PP/PS blends. Our previous work has demonstrated that zeolite 5A could be used as both a reinforcing filler and physical compatibilizer for PE/TPS blend (Thipmanee & Sane, 2012), to avoid relatively expensive, complicated, and time-consuming syntheses of chemical compatibilizers.

Thus based on prior literature results, it is evident that there are no systematic studies on the effect of incorporation sequence of zeolites on ternary polymer composites. In this work, zeolite ZSM-5 (ZSM5), composed of ten-membered tetrahedral rings with pore sizes of 5.2–5.7 Å, was incorporated into PE/TPS blend because this zeolite is hydrophobic (Shams-Ghahfarokhi & Nezamzadeh-Ejhieh, 2015) and has not been used in polymer compounding. Therefore, the

objective of this work was to investigate the effect of ZSM5 incorporation sequences on the phase morphology, microstructure and performance of PE/TPS films prepared by blown-film extrusion.

2. Materials and methods

2.1. Materials

Linear low-density polyethylene (PE, grade LL7410D1) with a melt-flow index (MFI) of 0.98 g/10 min (190 °C, 2.16 kg) was purchased from PTT Polymer Marketing (Thailand). Zeolite ZSM-5 ($\text{Na}_n\text{Al}_n\text{Si}_{96-n}\text{O}_{192}\cdot 16\text{H}_2\text{O}$, where $0 < n < 27$, ZSM5) with a Si/Al ratio of 100 was purchased from Zibo Xinhong Chemical (China). Glycerol (99.5% purity) was purchased from Siam Chemicals Solutions (Thailand). Hydrochloric acid solution (37%) was purchased from Merck (Germany). Cassava starch (13.2 wt% moisture content) was obtained from Tong Chan (Thailand). Amylose, protein, lipid, and ash contents of cassava starch determined according to Chrastil (1987) and AACC methods 30-10, 44-15A, and 46-11A were 15.7, 0.1, 0.2, and 0.2 wt%, respectively, and the amylose to amylopectin ratio was 16:84.

2.2. Preparation of PE/TPS/ZSM5 composite films

Two processing routes were used for preparing PE/TPS/ZSM5 composite pellets: (SI) melt compounding of PE with ZSM5 was carried out before incorporating into TPS; and (SII) TPS was compounded with ZSM5 prior to blending with PE.

Sequence I (SI): PE/ZSM5 + TPS

Prior to extrusion, PE and ZSM5 were dried in a hot-air oven at 60 °C (24 hrs) and 130 °C (3 hrs), respectively. Pre-mixed PE/ZSM5 composites were prepared by melt compounding PE with ZSM5 using a co-rotating, fully intermeshing twin-screw extruder (LTE-20-40, Labtech Engineering, Thailand) with a screw diameter of 20 mm and screw length to diameter (L/D) ratio of 40:1 at a temperature range of 80–160 °C and screw speed of 175 rpm. The PE/ZSM5 extrudate was cut into pellets by a pelletizer (LZ-120 pelletizer, Labtech Engineering). For TPS preparation, cassava starch was mixed with glycerol (weight ratio of 100:27) for 30 min using a 20-L mixer (Mitsubishi, Japan). The obtained mixture was extruded into pellets using the same twin-screw extruder at a screw speed of 175 rpm and extrusion temperature range of 80–160 °C. To prepare SI composites, the TPS and PE/ZSM5 pellets were melt blended and extruded into pellets using the same extruder at a temperature range of 80–140 °C and screw speed of 180 rpm. The concentrations of ZSM5 in SI composites were 1, 3, and 5 wt% (SI–1%, SI–3%, and SI–5%), with a constant weight ratio of PE to TPS of 70:30. The compositions used for preparing SI composites are summarized in Table 1.

Sequence II (SII): TPS/ZSM5 + PE

Prior to compounding, PE and ZSM5 were dried in a hot-air oven at 60 °C (24 hrs) and 130 °C (3 hrs), respectively. Pre-mixed TPS/ZSM5 composites were prepared by mixing ZSM5 with starch and glycerol using a starch to glycerol weight ratio of 100:27. The mixtures were extruded into pellets using the above mentioned twin-screw extruder at a temperature range of 80–160 °C and screw speed of 175 rpm. The obtained TPS/ZSM5 pellets were blended with PE, with a constant PE to TPS weight ratio of 70:30, to obtain polymer blend composites with ZSM5 concentrations of 1, 3, and 5 wt% (SII–1%, SII–3%, and SII–5%). Extrusion was performed at a

temperature range of 80–140 °C and screw speed of 180 rpm. All the constituents used in SII composite preparation are given in Table 1.

Finally, PE/TPS/ZSM5 composite pellets prepared via SI and SII sequences were converted into films by blown film extrusion using a single-screw extruder (LE25-30/C, Labtech Engineering), with a screw diameter of 25 mm and L/D ratio of 30:1, equipped with a film-blowing attachment unit (LF-400, Labtech Engineering). Blown film extrusion was carried out at a temperature range of 160–180 °C, screw speed of 45 rpm, blow-up ratio of 2.1, and take-off speed of 4.3 m/min. The range of average film thickness was 40–60 µm.

Table 1

Samples and constituents of PE/TPS/ZSM5 composites.

Samples	Overall constituents (wt%)			SI compositions (wt%)		SII compositions (wt%)	
	ZSM5	PE	TPS	Pre-mixed PE/ZSM5	TPS	Pre-mixed TPS/ZSM5	PE
PE	–	100	–	–	–	–	–
TPS	–	–	100	–	–	–	–
PE/TPS	–	70	30	–	–	–	–
SI–1%	1	69.3	29.7	70.3	29.7	–	–
SI–3%	3	67.9	29.1	70.9	29.1	–	–
SI–5%	5	66.5	28.5	71.5	28.5	–	–
SII–1%	1	69.3	29.7	–	–	30.7	69.3
SII–3%	3	67.9	29.1	–	–	32.1	67.9
SII–5%	5	66.5	28.5	–	–	33.5	66.5

2.3. Characterization and testing

2.3.1. Scanning electron microscopy

PE/TPS/ZSM5 stands were fractured after freezing in liquid nitrogen, and the microstructure of fracture surfaces was observed by scanning electron microscopy (FESEM, Hitachi S-4700, Japan) at an accelerating voltage of 10 kV. To examine the distributions of ZSM5 and TPS dispersed phases, the composite films were extracted with an aqueous hydrochloric acid solution (6 N) (Huneault & Li, 2012) for 3 weeks to remove TPS dispersed phase. All SEM specimens were mounted on aluminum stubs using double-sided adhesive carbon tape, dried at ambient temperature for ~2 days and then sputter-coated with platinum before imaging.

Energy dispersive spectroscopy (EDS) mapping of composite films was also carried out to determine the distributions of silicon and oxygen elements by using a scanning electron microscope (FEI Quanta FEG 450, The Netherlands) with an attachment of Oxford SDD Inca X-Max 50 energy dispersive spectroscopy operated at 10 kV and scanning time of 300 s.

2.3.2. *Melt rheological behavior*

Melt viscosity of pre-mixed composites (PE/ZSM5 and TPS/ZSM5) was measured using a capillary rheometer (RH7, Malvern Instruments, UK). Measurements were carried out at 170 °C (Kaseem, Hamad, & Deri, 2012) over a shear rate range of 100–5000 s⁻¹. The capillary diameter and length were 1 and 16 mm, respectively. Rheological properties were calculated using Bagley correction for end effects and Rabinowitsch correction for true shear rate.

2.3.3. *X-ray diffraction*

X-ray diffraction (XRD) of composite films was carried out with Cu K α radiation ($\lambda = 0.154$ nm) operating with a current of 30 mA and accelerating voltage of 40 kV (D8 Advance, Bruker, Germany). All samples were scanned over a range of 5–40° at a rate of 0.03°/s and the degree of

crystallinity of PE in PE/TPS/ZSM5 composites was determined using a method described by Mihai, Huneault, Favis, & Li (2007).

2.3.4. *Differential scanning calorimetry*

Thermal transitions (i.e. glass transition and melting) of PE/TPS/ZSM5 films were determined using a differential scanning calorimeter (DSC1 STARe, Mettler-Toledo, Switzerland). Samples were heated from –60 to 270 °C at a rate of 10 °C/min (Stagner, Alves, Narayan, & Beleia, 2011) and then cooled down to –60 °C at a rate of 20 °C/min under a nitrogen atmosphere. The degree of crystallinity of PE in PE/TPS/ZSM5 composites was calculated using Eq. (1):

$$\text{Degree of crystallinity (\%)} = \Delta H_m / \Delta H_m^o \times 100 / w \quad (1)$$

where ΔH_m is the melting enthalpy of PE in composite sample, ΔH_m^o is the melting enthalpy of 100% crystalline PE ($\Delta H_m^o = 288 \text{ J/g}$) (Luyt & Hato, 2005), and w is the weight fraction of PE in the sample.

2.3.5. *Tensile testing*

Tensile properties of PE/TPS/ZSM5 films were measured according to the ASTM D882-12 method at a crosshead speed of 5.08 cm/min (series 900, Applied Test Systems, USA). The films were cut into rectangular shape (13 mm wide and 114 mm long) and tested using 50-mm gauge length. To obtain compliance-corrected Young's modulus, 13 mm-wide rectangular samples with gauge lengths of 50, 102, and 203 mm were tested. Prior to tensile measurements, the samples were stored in a controlled humidity chamber (50% RH) at 25 °C for ~2 days. At least five replicates for each sample were tested.

2.3.6. *Impact testing*

The dropped-dart impact strength of PE/TPS/ZSM5 films was measured using a 12.7 mm hemispherical head and drop height of 254 mm (Dynatup 8200, Instron, USA) in accordance with ASTM D3763. Film samples were cut into rectangular shape ($90 \times 114 \text{ mm}^2$). Impact testing was performed using multiple layers of films (8, 16, and 20). At least five replicates were tested for each sample.

2.4. *Statistical analysis*

The data were statistically evaluated using the one-way analysis of variance (ANOVA) and the significant difference ($p \leq 0.05$) between mean values was determined with the Duncan's new multiple-range test using SPSS Statistics Version 10.0.

3. Results and discussion

3.1. Phase morphology of PE/TPS/ZSM5 composites

Fig. 1 illustrates SEM images of fracture surfaces of PE/TPS/ZSM5 composite strands in comparison with those of PE, TPS, and PE/TPS blend. The fracture surfaces of both PE and TPS were smooth and homogeneous. However, after melt blending PE with TPS (70:30), the blend was phase separated due to the hydrophobicity of PE and hydrophilicity of TPS, causing the formation of PE-rich continuous phase and TPS-rich dispersed phase with round shape and sizes ranging from ~ 1.5 to $5 \text{ }\mu\text{m}$. Incorporating ZSM5 (1–5 wt%) into PE/TPS blend via SI route (compounding of PE with ZSM5 prior to melt blending with TPS) slightly improved the

216 dispersion of TPS and resulted in decreased dispersed domain size to ~1–3 μm . At high ZSM5
217 loading (i.e., SI–5%), zeolite agglomerates (<10 μm) were observed in the continuous phase of
218 PE/TPS blend. ZSM5 particles were found to physically disperse in PE/TPS matrix, according to
219 the results obtained from Fourier Transform Infrared (FTIR) spectroscopy analysis (Fig. S1,
220 Supplementary data). The dispersion of TPS was more improved and the size of TPS domains
221 was further reduced to 0.5–2 μm when ZSM5 was incorporated into PE/TPS blend through SII
222 (compounding TPS with ZSM5 prior to melt blending with PE). Furthermore, increasing ZSM5
223 content to 3–5 wt% continued to improve the spatial distribution of TPS and decreased the size
224 of TPS dispersed phase while increased the volume fraction of continuous phase in PE/TPS
225 blend, indicating that the degree of mixing between PE and TPS increased with increasing ZSM5
226 content.

Fig. 1. SEM micrographs of fracture surfaces of PE, TPS, PE/TPS, and PE/TPS/ZSM5 extruded strands.

To observe the ZSM5 distribution and film microstructure, the composite films were extracted with an aqueous hydrochloric acid solution (6 N) to remove the TPS dispersed phase prior to SEM characterization. Fig. 2 illustrates SEM micrographs of ZSM5 particles and films of PE/TPS blend and PE/TPS/ZSM5 composites. ZSM5 particles were irregular in shape and size, and were agglomerated with size ranging from 2 to 8 μm . PE/TPS film displayed a large

236 population of micron-sized round holes of the previously existing TPS dispersed phase. The
237 domain size of the dispersed phase decreased in composites containing 1 wt% of ZSM5,
238 especially in SII-1% composite. Likewise, increasing the ZSM5 content to 3 wt% also resulted
239 in a further decrease in the size of the discontinuous phase. Moreover, the dispersed domains
240 tended to preferentially align in the machine direction, forming interconnecting elongated TPS
241 domains. However, this orientation was less obvious in composites containing ZSM5 content of
242 5 wt%, possibly because the presence of a large number of ZSM5 particles limits the mobility
243 and hence the orientation of the TPS dispersed phase along the machine direction. In addition,
244 the size of the TPS phase in SI composites increased as the amount of ZSM5 was increased
245 (from 3 to 5 wt%). Nonetheless, the size of dispersed domains in SII composites still remained
246 approximately the same (see Fig. 2). Therefore, the ZSM5 incorporation route plays a great role
247 in controlling PE/TPS blend morphology, and incorporating zeolite via SII promotes the
248 dispersive mixing between PE and TPS. Moreover, the results suggest that ZSM5 particles
249 migrate from TPS dispersed domain toward PE continuous phase during sequence II melt
250 blending, whereas the majority of ZSM5 still remains within the PE phase when melt blending is
251 conducted via sequence I. To confirm these findings, EDS analysis was performed to trace the
252 distributions of ZSM5 and TPS by mapping of silicon and oxygen elements in unextracted SI
253 and SII films. Silicon map displayed the distribution of ZSM5; whereas, oxygen map traced both
254 the locations of ZSM5 and TPS. Fig. 3 shows EDS composition maps of silicon and oxygen
255 elements in comparison with their corresponding SEM images of SI-5% and SII-5% samples.
256 For SI-5%, comparison between silicon and oxygen maps revealed that ZSM5 particles were
257 distributed throughout the film surface without selective localization in TPS dispersed phase.
258 Similar trend was also observed for SII-5%, hence confirming the migration of ZSM5 from TPS

dispersed phase to PE matrix. Moreover, TPS dispersed domains were more uniformly distributed throughout the film when compared to SI-5% composite, in agreement with the results obtained from Atomic Force Microscopy (AFM) analysis (Fig. S2, Supplementary data). This could be explained by (i) the higher affinity (Elias et al., 2007 and Jarntong et al., 2012) between PE and ZSM5 compared to that of TPS and ZSM5 and (ii) the decrease in viscosity of TPS dispersed phase (Xu, Qin, Yu, Huang, Zhang, & Ruan, 2015) after incorporation of ZSM5.

Fig. 2. SEM micrographs of ZSM5 particles and films of PE/TPS blend and PE/TPS/ZSM5 composites after selective removal of TPS dispersed phase by extraction of film samples with an aqueous hydrochloric acid solution (6 N).

Fig. 3. SEM images and EDS composition distribution maps of silicon and oxygen elements in unextracted SI-5% and SII-5% composite films.

3.2. Rheological behavior of pre-mixed PE/ZSM5 and TPS/ZSM5 composites

In melt blending process of PE/TPS/ZSM5 composites, the size of dispersed phase is not only controlled by the chemical affinity between ZSM5 and pre-mixed polymers but also the viscosity of pre-mixed composites (PE/ZSM5 and TPS/ZSM5). To evaluate the effect of ZSM5 on the viscosity of matrix and dispersed phases, the viscosity of PE/ZSM5 and TPS/ZSM5 composites was determined in comparison with that of TPS and PE. The viscosity curves of PE, TPS, and pre-mixed PE/ZSM5 and TPS/ZSM5 composites used in preparation of SI-5% and SII-5% composites are shown in Fig. 4. It was found that compounding with ZSM5 decreased the viscosity of TPS while increased the viscosity of PE. The decrease in viscosity of TPS facilitates

the breakup of TPS/ZSM5 droplets (Xu et al., 2015) during mixing with PE in a twin-screw extruder. During this step, migration of ZSM5 from TPS dispersed phase to PE matrix also occurred due to the affinity between ZSM5 and PE, further leading to smaller TPS dispersed domains obtained in SII composites (Figs. 1–3). On the contrary, in SI sequence, the majority of ZSM5 still remained in PE matrix and the improvement in distributive mixing between PE and TPS could not be achieved.

Fig 4. Viscosity of pre-mixed PE/ZSM5 and TPS/ZSM5 composites shown in comparison with PE and TPS viscosity.

3.3. Microstructure of PE/TPS/ZSM5 composites

X-ray diffraction (XRD) analysis was carried out to determine the effect of ZSM5 and its incorporation sequence on the crystallinity of PE/TPS/ZSM5 composites. Fig. 5 shows XRD patterns of PE/TPS/ZSM5 composites prepared via SI and SII sequences in comparison with those of ZSM5, PE, and PE/TPS blend. ZSM5 exhibited main characteristic peaks at 2θ ranges of $7.9\text{--}8.7^\circ$ and $23.0\text{--}23.9^\circ$, in agreement with those previously reported by Chen, Zhang, & Yan (2012). The major characteristic peak of PE appeared at 2θ of 21.5° (Shafiq, Yasin, & Saeed, 2012). For TPS, two primary diffraction peaks were observed at 2θ of 13.3 and 21.1° , corresponding to V_A -type crystalline structure (Corradini, de Carvalho, da Silva Curvelo, Agnelli, & Mattoso, 2007). After melt blending with PE, the characteristic peak of TPS at 2θ of 13.3° was concealed by the PE amorphous domain, and the peak of TPS at 2θ of 21.1° overlapped with the peak of the PE crystalline portion. When incorporating ZSM5 (1–5 wt%) into PE/TPS blend via SI and SII, the composites still exhibited the main characteristic peaks similar to those of PE/TPS blend and ZSM5 (Fig. 5).

The crystallinity of SI composites was higher than that of PE/TPS blend (35.3%) and increased from 38.8 to 59.5% when increasing ZSM5 content from 1 to 5 wt% (Table 2), indicating that ZSM5 acts as a nucleating agent for PE and further confirming the existence of ZSM5 in PE matrix (see also Figs. 1–3). The crystallinity of PE in SII composites (47.5–53.1%) was also higher than that of PE/TPS blend, indicating that ZSM5 migrates from TPS to PE phase and acts as a nucleating agent for PE. However, the crystallinity of PE in the SII composites decreased from 53.1 to 47.5%, when increasing zeolite content from 1 to 5 wt%, indicating that the improved distributive mixing between PE and TPS reduces the crystallization of PE.

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319

320 **Fig. 5.** X-ray diffraction patterns of PE/TPS/ZSM5 composite films shown in comparison with
 321 those of ZSM5, PE, TPS, and PE/TPS blend.

322

Table 2

Crystallinity and mechanical properties of PE, PE/TPS blend, and PE/TPS/ZSM5 composites.

Samples	Crystallinity (%)		Tensile strength (MPa)	Elongation at break (%)	Compliance-corrected Young's modulus (MPa)	Impact strength (kJ/m)
	XRD	DSC				
PE	41.4 ± 1.9 ^c	40.7 ± 0.9 ^c	32.0 ± 3.4 ^a	509 ± 15 ^a	358	4.09 ± 0.03 ^a
PE/TPS	35.3 ± 1.8 ^g	34.5 ± 0.4 ^e	20.6 ± 1.9 ^b	245 ± 10 ^c	158	1.74 ± 0.04 ^d
SI-1%	38.8 ± 0.7 ^f	41.7 ± 3.2 ^{bc}	12.9 ± 1.9 ^c	229 ± 13 ^c	409	1.87 ± 0.05 ^c
SI-3%	49.1 ± 0.1 ^c	44.6 ± 1.3 ^b	11.6 ± 1.6 ^c	175 ± 19 ^d	410	1.11 ± 0.11 ^c
SI-5%	59.5 ± 1.6 ^a	48.3 ± 0.6 ^a	11.9 ± 2.1 ^c	106 ± 9 ^e	412	1.26 ± 0.08 ^e
SII-1%	53.1 ± 1.0 ^b	41.4 ± 2.3 ^{bc}	21.1 ± 0.9 ^b	444 ± 26 ^b	446	2.03 ± 0.11 ^b
SII-3%	51.2 ± 1.5 ^{bc}	44.7 ± 1.1 ^b	21.9 ± 2.2 ^b	436 ± 27 ^b	571	2.07 ± 0.09 ^b
SII-5%	47.5 ± 1.7 ^d	38.4 ± 1.0 ^d	23.8 ± 1.3 ^b	407 ± 10 ^b	600	2.10 ± 0.11 ^b

* Different superscript letters indicate significant differences ($p \leq 0.05$).

3.4. Thermal properties of PE/TPS/ZSM5 composites

DSC **curves** of PE, TPS, PE/TPS blend, and PE/TPS/ZSM5 composites are illustrated in Fig. 6. The glass-transition temperature (T_g) of TPS occurred at a temperature of 52 °C. However, we were unable to observe the T_g of PE because the transition temperature was below the DSC instrument cooling limit (−80 °C). After melt blending PE with TPS, T_g of TPS decreased by ~5 °C. With the addition of ZSM5 to the PE/TPS blend via both SI and SII, T_g of TPS further decreased by ~2–5 °C, possibly because the presence of ZSM5 could increase the chain mobility of PE and TPS.

The two endothermic transitions of the PE/TPS blend observed at temperatures of 122 and 199 °C correspond to melting points (T_m s) of PE and TPS (Arboleda, Montilla, Villada, & Varona, 2015), respectively (Fig. 6). Incorporating ZSM5 through SI and SII had no effect on T_m

of PE. However, T_m of TPS significantly changed, depending on the zeolite incorporation sequence. T_m of TPS in the blend increased from 199 to 262 and 219 °C in SI-1% and SII-1% composites, respectively. However, increasing zeolite content from 1 to 3–5 wt% resulted in decreased T_m of TPS, from 262 to 243–251 °C for SI composites and from 219 to 163–164 °C for SII composites. Note that the obtained melting temperatures were lower than the onset of thermal degradation of TPS (270–273 °C), as determined by Thermogravimetric Analysis (TGA) (Fig. S3, Supplementary data). T_m of TPS dramatically decreased when ZSM5 (3–5 wt%) was incorporated into the PE/TPS blend via SII, implying that incorporation of zeolite into TPS prior to blending with PE improves the distributive mixing between PE and TPS (Pereira, Paulino, Rubira, & Muniz, 2010), as was illustrated by SEM/EDS images in Figs.1–3.

The crystallinity of PE was estimated by DSC in order to confirm the crystallinity change in SI and SII composites determined by XRD analysis. The ranges of PE crystallinity of SI and SII composites, determined from the measurements of enthalpy of melting of PE, were 41.7–48.3% and 38.4–44.7%, respectively (Table 2). The PE crystallinity of SI composites increased with ZSM5 content; whereas, that of SII composites tended to decrease with increasing zeolite content, in agreement with XRD results (Table 2), suggesting that the nucleating effect of ZSM5 on PE was lessened by the improved distributive mixing between PE and TPS. The different values of crystallinity were obtained from DSC and XRD analyses primarily due to the difference in principles of measurements for estimating crystallinity content used in each method: enthalpy of fusion for DSC and three-dimensional order for XRD.

Upon cooling the PE/TPS blend and PE/TPS/ZSM5 composites down to a temperature of –60 °C (data not shown), only crystallization temperature (T_c) of PE was observed at a temperature range of ~106–108 °C, indicating that ZSM5 incorporation sequence and content have no effects

on the T_c of PE. For TPS, T_c was not observed in accordance with that previously reported by Stagner et al. (2011) possibly because: (i) TPS crystallization (V_A -type amylose-glycerol complexes) slowly occurs during storage, and this structure is destroyed upon melting and cannot be retrieved by melt crystallization during sample cooling in DSC equipment; and (ii) the major constituent of starch is high-molecular-weight amylopectin and its crystallization rate is very slow (Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998).

Fig. 6. DSC curves of PE/TPS/ZSM5 composite films shown in comparison with those of PE, TPS, and PE/TPS blend.

3.5. Tensile properties of PE/TPS/ZSM5 composites

Table 2 displays tensile properties (tensile strength, compliance-corrected Young's modulus, and elongation at break) and impact strength of PE, PE/TPS blend, and PE/TPS/ZSM5

377 composite films prepared by different zeolite incorporation sequences. Tensile strength,
378 modulus, and elongation at break of PE were 32.0 MPa, 358 MPa, and 509%, respectively. Melt
379 blending of PE with 30 wt% of TPS resulted in significantly decreased tensile strength, modulus,
380 and elongation at break of PE to 20.6 MPa, 158 MPa, and 245%, respectively (Table 2). This can
381 be explained by the blend immiscibility (Figs. 1 and 2), likely due to the poor interfacial
382 adhesion between nonpolar PE and highly polar TPS (Cerclé et al., 2013). With an addition of 1
383 wt% of ZSM5 to the PE/TPS blend by SI sequence (SI-1%), tensile strength of the blend
384 significantly decreased by ~40%, whereas the compliance-corrected blend modulus increased by
385 1.6 times, without significantly affecting the elongation at break. Increasing zeolite content from
386 1 to 3 and 5 wt% dramatically decreased the elongation at break of SI-1% composite from 229
387 to 175 and 106%, respectively, without significant effect on tensile strength and modulus of SI
388 composites (Table 2). Accordingly, tensile strength and elongation at break of PE/TPS blend
389 substantially diminished after incorporating ZSM5 via SI and the decrease in flexibility of SI
390 composite films with increasing zeolite content could be primarily caused by the increase in TPS
391 dispersed phase size and agglomeration of ZSM5 particles (see Fig. 2). However, the opposite
392 trends were observed for SII composites as their tensile properties were considerably improved
393 compared to those of PE/TPS blend and SI composites. Incorporating 1 wt% of ZSM5 by SII
394 sequence (SII-1%) significantly increased elongation at break of the blend from 245 to 444%
395 (almost the same as neat PE) and compliance-corrected modulus of the blend from 158 to 446
396 MPa, without significantly affecting its tensile strength (Table 2). The increases in both
397 elongation at break and modulus of SII-1% composite could be principally attributed to: (i) the
398 improved dispersion of TPS and mixing of PE/TPS blend (Thipmanee & Sane, 2012); and (ii)
399 the reinforcing effect of ZSM5 in PE/TPS blend (Pastor et al., 2012).

Changing zeolite content had no significant effect on the tensile strength and elongation at break of SII composites (see Table 2). Although, some ZSM5 particles were agglomerated in SII–5% composite (Fig. 2), its strength and flexibility were still approximately the same as those of SII–1% and SII–3% composites. The results imply that the improved mixing between PE and TPS in SII composites is achieved by increasing the content of ZSM5. Furthermore, our tensile results suggest that compounding TPS with ZSM5 prior to blending with PE (SII) is a more effective alternative to improve the flexibility and toughness of PE/TPS blend than in the case of compounding PE with ZSM5 prior to melt blending with TPS (SI).

3.6. Impact strength of PE/TPS/ZSM5 composites

The effects of ZSM5 incorporation sequence and content on the normalized impact energy (impact strength) of PE/TPS/ZSM5 composites in comparison with those of PE and PE/TPS blend are displayed in Table 2. Impact strength of PE was 4.09 kJ/m; however, after melt blending PE with TPS (70:30 wt/wt), its impact strength considerably decreased to 1.74 kJ/m. Incorporating ZSM5 (1–5 wt%) through SII improved the impact strength of the PE/TPS blend to 2.03–2.10 kJ/m. However, compared to each other, impact strength of SII composites containing 1–5 wt% of ZSM5 were not significantly different. In contrast, incorporating 1 wt% of zeolite via SI only slightly increased the impact strength of the PE/TPS blend, from 1.74 to 1.87 kJ/m. Increasing ZSM5 content to 3 and 5 wt% resulted in a significant decrease in impact strength to 1.11 and 1.26 kJ/m. Additionally, impact strength of SII composites was significantly higher than that of SI composites, proving further that compounding of TPS with ZSM5 prior to

blending with PE (SII) efficiently improves the spatial distribution of TPS in the blend matrix, in agreement with SEM/EDS (Figs. 1–3) and tensile (Table 2) results.

4. Conclusions

The incorporation sequence of ZSM5 plays a great role in determining the distributive mixing and properties of PE/TPS/ZSM5 composites. Significantly improved mixing and mechanical properties of composites were achieved when ZSM5 was incorporated into TPS during starch plasticization stage before blending with PE (SII). In contrast, when mixing ZSM5 with PE prior to blending with TPS (SI), the presence of ZSM5 did not improve the mixing and performance of PE/TPS/ZSM5 composites. Enhanced mixing and performance of PE/TPS blend through SII route occurred because ZSM5 has higher affinity to PE than TPS and compounding with ZSM5 reduced the viscosity of TPS, facilitating the migration of ZSM5 toward PE matrix and the breakup of TPS dispersed phase during melt blending. Furthermore, the crystallization of PE due to nucleating effect of ZSM5 was hindered by the improved distributive mixing between PE and TPS. Our results suggest that pre-mixing ZSM5 with TPS, in the same step of starch plasticization, before blending with PE is a more effective and economical route to improve the mixing and performance of PE/TPS blend. Finally, this alternative could be practically implemented at industrial scale to manufacture PE/TPS blend.

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Figures and Tables Captions

Fig. 1. SEM micrographs of fracture surfaces of PE, TPS, PE/TPS, and PE/TPS/ZSM5 extruded strands.

Fig. 2. SEM micrographs of ZSM5 particles and films of PE/TPS blend and PE/TPS/ZSM5 composites after selective removal of TPS dispersed phase by extraction of film samples with an aqueous hydrochloric acid solution (6 N).

Fig. 3. SEM images and EDS composition distribution maps of silicon and oxygen elements in unextracted SI-5% and SII-5% composite films.

Fig 4. Viscosity of pre-mixed PE/ZSM5 and TPS/ZSM5 composites shown in comparison with PE and TPS viscosity.

Fig. 5. X-ray diffraction patterns of PE/TPS/ZSM5 composite films shown in comparison with those of ZSM5, PE, TPS, and PE/TPS blend.

Fig. 6. DSC **curves** of PE/TPS/ZSM5 composite films shown in comparison with those of PE, TPS, and PE/TPS blend.

Table 1. Samples and constituents of PE/TPS/ZSM5 composites.

Table 2. Crystallinity and mechanical properties of PE, PE/TPS blend, and PE/TPS/ZSM5 composites.

Samples	Overall constituents (wt%)			SI compositions (wt%)		SII compositions (wt%)	
	ZSM5	PE	TPS	Pre-mixed PE/ZSM5	TPS	Pre-mixed TPS/ZSM5	PE
PE	–	100	–	–	–	–	–
TPS	–	–	100	–	–	–	–
PE/TPS	–	70	30	–	–	–	–
SI–1%	1	69.3	29.7	70.3	29.7	–	–
SI–3%	3	67.9	29.1	70.9	29.1	–	–
SI–5%	5	66.5	28.5	71.5	28.5	–	–
SII–1%	1	69.3	29.7	–	–	30.7	69.3
SII–3%	3	67.9	29.1	–	–	32.1	67.9
SII–5%	5	66.5	28.5	–	–	33.5	66.5

Table 1. (Thipmanee, Lukubira, Ogale, & Sane)

Samples	Crystallinity (%)		Tensile strength (MPa)	Elongation at break (%)	Compliance-corrected Young's modulus (MPa)	Impact strength (kJ/m)
	XRD	DSC				
PE	41.4 ± 1.9 ^e	40.7 ± 0.9 ^c	32.0 ± 3.4 ^a	509 ± 15 ^a	358	4.09 ± 0.03 ^a
PE/TPS	35.3 ± 1.8 ^g	34.5 ± 0.4 ^e	20.6 ± 1.9 ^b	245 ± 10 ^c	158	1.74 ± 0.04 ^d
SI-1%	38.8 ± 0.7 ^f	41.7 ± 3.2 ^{bc}	12.9 ± 1.9 ^c	229 ± 13 ^c	409	1.87 ± 0.05 ^c
SI-3%	49.1 ± 0.1 ^c	44.6 ± 1.3 ^b	11.6 ± 1.6 ^c	175 ± 19 ^d	410	1.11 ± 0.11 ^e
SI-5%	59.5 ± 1.6 ^a	48.3 ± 0.6 ^a	11.9 ± 2.1 ^c	106 ± 9 ^e	412	1.26 ± 0.08 ^e
SII-1%	53.1 ± 1.0 ^b	41.4 ± 2.3 ^{bc}	21.1 ± 0.9 ^b	444 ± 26 ^b	446	2.03 ± 0.11 ^b
SII-3%	51.2 ± 1.5 ^{bc}	44.7 ± 1.1 ^b	21.9 ± 2.2 ^b	436 ± 27 ^b	571	2.07 ± 0.09 ^b
SII-5%	47.5 ± 1.7 ^d	38.4 ± 1.0 ^d	23.8 ± 1.3 ^b	407 ± 10 ^b	600	2.10 ± 0.11 ^b

* Different superscript letters indicate significant differences ($p \leq 0.05$).

Table 2. (Thipmanee, Lukubira, Ogale, & Sane)

Figure(s)

Fig. 1. (Thipmanee, Lukubira, Ogale, & Sane)

Fig. 2. (Thipmanee, Lukubira, Ogale, & Sane)

Fig. 3. (Thipmanee, Lukubira, Ogale, & Sane)

Fig. 4. (Thipmanee, Lukubira, Ogale, & Sane)

Fig. 5. (Thipmanee, Lukubira, Ogale, & Sane)

Fig. 6. (Thipmanee, Lukubira, Ogale, & Sane)