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Reactive PSU/PA blends: comparison of materials prepared by mini-twin screw extruder and batch mixer

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Abstract

The morphology and mechanical properties of non-reactive and reactive polyamide (PA)/polysulfone (PSU) blends prepared in a mini-twin screw extruder and a Haake batch mixer were investigated and compared using transmission electron microscopy and solvent extraction. In the reactive blend, few wt.% of phthalic anhydride-terminated PSU was added. The new mini-twin screw extruder, allowing the compounding of laboratory products starting from 150 g, is efficient in producing homogenous dispersion in both non-reactive and reactive PSU/PA blends. In the reactive systems, PSU–PA copolymers in situ formed act as typical emulsifier to provide finer particle size and better morphology stability. Significant toughness improvement found in the reactive systems appears to originate from the enhanced interfacial adhesion provided by the PSU–PA copolymers, not simply by the reduced particle size of PA dispersed phases. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Reactive blending; Mixer; Morphology

1. Introduction

Reactive polymer blending is currently the most common compatibilization method used in industry to develop new materials [1]. Copolymer generated by chemical reactions of functionalized chains at polymer/polymer melt interface can improve the microstructure and properties of polymer blends, promote smaller droplet size by retarding particle coalescence, and increase the interfacial fracture toughness [2–6].

To increase the rather limited number of applications for high performance polymers like polysulfones (PSU), polyethersulfones, and polyetherimides, blends with engineering thermoplastics like polyamides (PA), polyesters or polycarbonates are of high potential. PSU is a typical amorphous polyarylether, which offers high heat resistance, nice dimensional stability, and good mechanical properties. However, owing to their chemical structure, it has low stress crack resistance and high melt viscosity. Such major drawbacks could be overcome by blending with a semi-crystalline polymer like PA. The PSU/PA blends may be interesting materials for automotive and electrical applications.

Recent studies on melt mixing of reactive PSU/PA blends (PA is major component) were done mainly in a gram-scale mixer, the Mini-Max moulder [7–12]. This miniature mixer is quite useful for the fundamental study of morphology development during melt processing since it is easy to open and sampling materials at different times [13]. The mixer is effective in mixing low-molecular weight non-reactive and equivalent reactive polymers. However, the mixing capability of the miniature mixer may be reduced when the melt viscosity and elasticity of major component or blends are relatively high i.e., the good homogeneity of the blend is slowly obtained [14], although adding steel balls into the mixer could improve dispersion [15]. Because of the mentioned drawback, the Mini-Max moulder do not appear to be an appropriate mixer for the study of PSU/PA or PSU/PA/rubber ternary blends when PSU used as a major component is commercial grade and has high melt viscosity (unpublished results).

Recently, a new mini-twin screw extruder PTW 16 (PTW = parallel twin screw, Haake) is available. The diameter of the screw is 16 mm and the free volume in the machine is very small. The minimum amount of material required to operate the PTW is about 250–500 g. This required quantity is much smaller than that required for other laboratory-extruder types, usually requires (2–5 kg).

In this study, we prepared a series of non-reactive and reactive PSU/PA blends using the mini-compounder PTW16 and the Haake batch mixer. PSU used is a commercial grade with rather high melt viscosity and a major

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component in the blend. In the reactive blend, few wt.% of reactive PSU, phthalic anhydride-terminated PSU (PSU–PhA), having comparable molecular weight with the non-reactive PSU was added. The morphology of the blends was investigated by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Digital image analysis was applied to analyse TEM or SEM picture. Then, influence of mixer types on the morphology and properties of the non-reactive and reactive PSU/PA blends were compared and discussed.

2. Experimental section

2.1. Materials

The PSU and PA used were commercial polymers of BASF Aktiengesellschaft, Ultrason® S2010 and Ultramid® T, respectively. PSU is a condensation product of Bisphenol-A and 4,4′-dichlorodiphenylsulfone. PA is partially aromatic polyamide consisting of units derived from ϵ-caprolactam, hexamethylene diamine, and terephthalic acid. PSU–PhA was prepared by addition of 4-fluorophthalic anhydride to the as-polymerized solution of PSU. The amount of anhydride end-groups was determined by FT–IR. Detail of preparation procedure has been given elsewhere [16]. Characteristics of the materials used are summarised in Table 1.

2.2. Melt mixing

To remove absorbed moisture, all polymers were vacuum dried at 80°C over night before blending. A mixture of non-reactive PSU and reactive PSU was melt blended with PA at a 70/30 (PSU/PA) wt. ratio using a batch mixer, Haake Rheomix 600 at 315°C. All materials were fed to the mixer in pellet form. Rotation speed was fixed at 50 rpm. At this rotor speed, the maximum drag flow, shear rate in the mixer is 65 s^{-1}. This can be estimated on the basis of the rotor speed and the minimum gap between the rotor tip and the mixing chamber wall. The mass of materials charged to the mixer was constant at 50 g. The mixing proceeded for 8 min.

The blends were prepared also using a mini-twin screw extruder PTW 16, operating at a barrel temperature 320°C with a screw speed of 150 rpm. The screw length-to-diameter ratio (L/D) is fixed at 25. The total throughput in all blends was 2 kg/h. The compositions of the prepared blend by the Hakke mixer and the PTW are given in Table 2.

Table 1
Characteristics of polymers used

Nomenclature	M_n [a]	M_w [a]	$\eta*$ [b]	Functionality[c]
PA	13,000	35,000	1500	50
PSU	12,000	30,000	1700	0
PSU–PhA	10,000	32,000		85

[a] By GPC measurement (g/mol).

[b] Complex melt viscosity at 310°C, frequency range 10–50 rad/s (Pa s).

[c] Content of functional group (μmol/g).

Table 2
Experiment runs and the results of image analysis

Blend no.	Mixer	Blend composition (wt%)			D_{EM} (μm)	S_{av}
		PA	PSU	PSU–PhA		
1	PTW	30	70	–	0.87	0.17
2	PTW	30	65	5	0.16	0.06
3	PTW	30	60	10	0.12	0.06
4	Haake	30	70	–	2.09	0.75
5	Haake	30	65	5	0.30	0.22
6	Haake	30	60	10	0.19	0.11

2.3. Morphology analysis

For TEM observation, the specimen was cryomicrotomed at −45°C by ultramicrotome (Reichert Ultracut-S). The ultrathin section of *ca*. 60 nm thickness was mounted on 200 mesh copper grid and exposed to the RuO_4 vapour for 20 min. The two-phase morphology was observed by transmission electron microscope, Zeiss EM 902, at an accelerating voltage of 100 kV.

TEM pictures were digitized using scanner. The area of an individual particle was directly determined using an appropriate software (analySIS 3.0, GmbH.). The diameter of dispersed particle D_i was calculated by $D_i = 2(a_i/\pi)^{1/2}$, assuming the circular shape of the particle. Then, we obtained an average:

$$D_{\mathrm{EM}}=\sum_{i=1}^{N} D_i^3 / \sum_{i=1}^{N} D_i^2$$

when N was 200–500 in a TEM picture.

2.4. Extraction procedure

About 6 g of each blend was immersed in 100 ml of N,N′-dimethylformamide (DMF) for the extraction of the PSU matrix phase. After 24 h, the suspension was separated into two phases by centrifugation at 14,000 rpm for 30 min. The transparent top phase (PSU in DMF) was collected. The bottom phase, insoluble materials (unreacted PA and PSU–PA copolymers), was dried and further extracted with formic acid (HCOOH), which acts as a selective solvent for the PA. The insoluble material was again separated and counted as in situ formed copolymer.

2.5. Mechanical test

The mini-injection-moulding machine (Boy 12 M) was used to prepare ISO-bar specimens for mechanical testing. It is worth to be noted that due to small screw diameter (14 mm), the mini-injection-moulding machine can produce regular ISO-specimens starting from 150-g materials. The

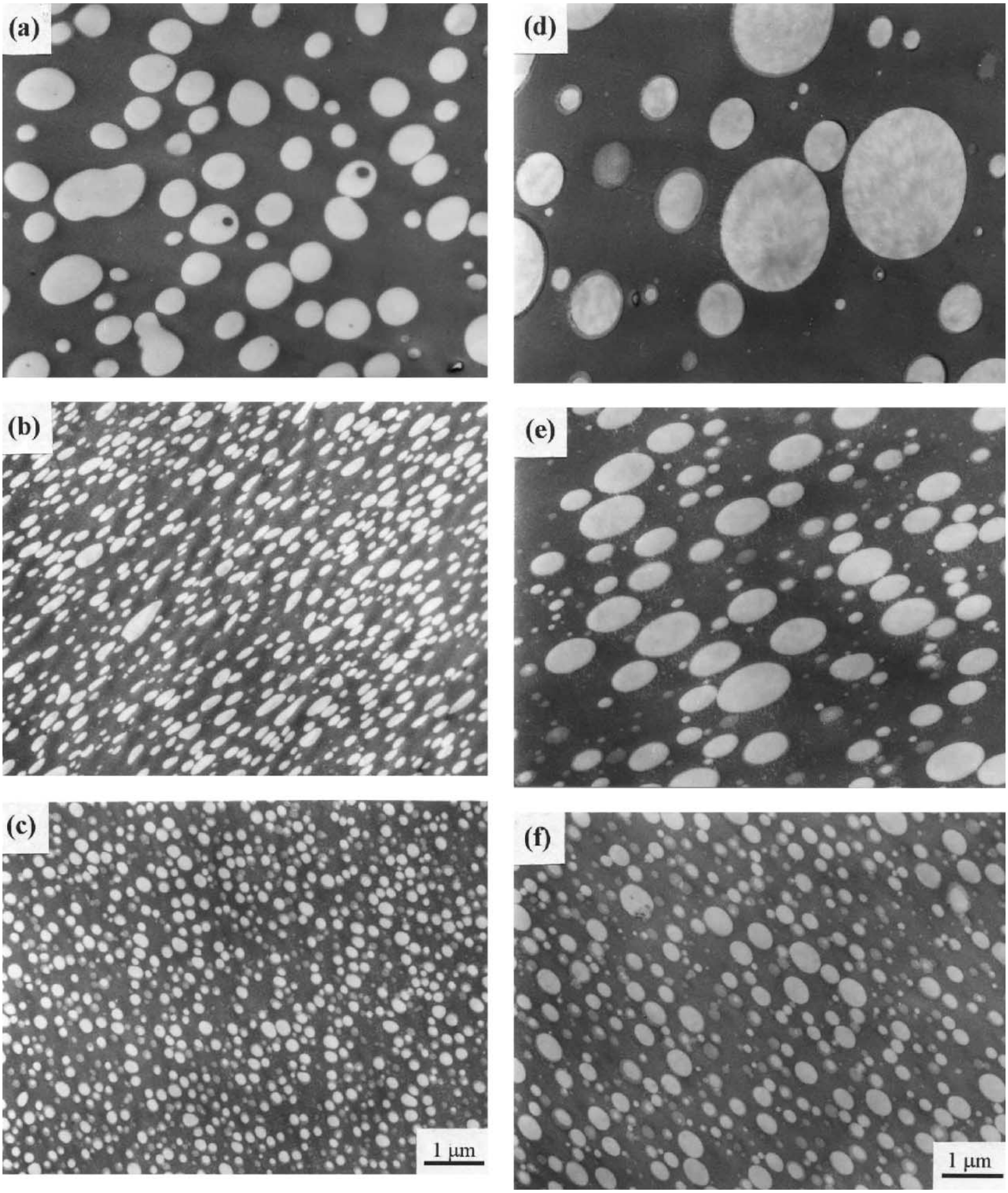

Fig. 1. TEM micrographs (RuO_4 stained) showing morphology of blends prepared by the PTW ((a)Bld1, (b) Bld2, (c) Bld3) and the Hakke batch mixer ((d) Bld4, (e) Bld5 and (d) Bld6).

specimens were injection moulded at 330°C and the mould temperature was 120°C. The mechanical testing of the materials was performed according to ISO 179-1eA and DIN 53457.

A melt volume index (MVI) capillary rheometer, (Göttfert, Werkstoff-Prüfmaschinen, Model MP-D) with a 2 mm in diameter cylindrical die was used to prepare the extrudate stands. About 4–5 g of materials was used. After preheating of the materials, the strand was extruded through the die into the bottom part. Stress–strain curves of the strand specimen were measured at room temperature by a tensile testing machine (Zwick Z010/TH2A) and five to seven specimens were tested for each material.

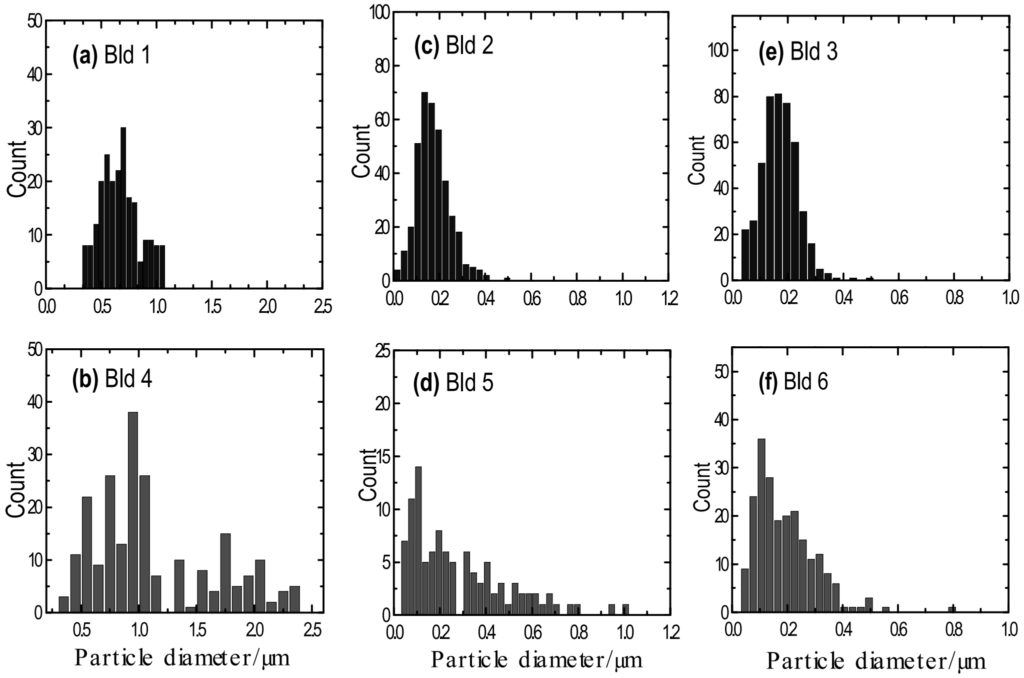

Fig. 2. Particle size distributions of equivalent diameter obtained by image analysis of TEM micrographs of (a) Bld1, (b) Bld2, (c) Bld3, (d) Bld4, (e) Bld5 and (f) Bld6.

3. Results and discussion

Fig. 1 shows TEM images of blends after 8-min mixing. The darker region corresponds to the PSU phase stained by RuO_4. It can be seen that tendency of the obtainable blend morphology between the blends prepared by the PTW (Fig. 1(a)–(c) and the Haake batch mixer (Fig. 1(d)–(f)) is similar. That is the dispersed phase sizes of the reactive blends (Fig. 1(b)–(c) and (e)–(f)) are finer than those of the non-reactive blends (Fig. 1(a) and (d)). This is due to the emulsifying effect of the PSU–PA copolymer in situ created at the interface by coupling reaction.

Quantitative information about the morphology in terms of the average particle size and particle size distribution can be obtained from the image analysis, as shown in Fig. 2. The results of the average particle size and standard deviation are summarised also in Table 2. It can be seen from Figs. 1 and 2 that at given processing conditions used in this study, the PTW is more effective in producing a homogenous dispersion, even in the non-reactive case. The particle size distributions of the non-reactive blend (Bld1) and the reactive blends (Bld2 and Bld3) prepared by the PTW are rather Gaussian shaped and quite narrow. In the reactive blends (Blds 2 and 3), there is no particle larger than 0.6 μm in diameter. In contrast, the Haake batch mixer gives somewhat poor dispersions and inhomogeneous in the non-reactive case Bld4 as evidence by the rather broad particle size distribution (Fig. 2(b)). However, the average particle size decreases and the particle size distribution becomes narrower as amounts of the reactive PSU, PSU–PhA, increase. At 10 wt.% of PSU–PhA, morphology of Bld 3 (Figs. 1(c) and 2(e)) and Bld 6 (Figs. 1(f) and 2(f)) prepared by the PTW and the Hakke batch mixer respectively are rather similar.

With the limited amount of the blends prepared by the Hakke mixer (less than 50 g), it is impossible to prepare and perform mechanical testing with the normal standard injection-moulded sample because the preparation of injection moulded samples usually requires several hundred grams to kilogram materials. Therefore, as an alternative way, the extrudate strand specimens were prepared and used to evaluate the mechanical performance of these blends.[1] In order to compare, the extrudate strand specimens of the blends prepared by the PTW were also prepared and tested. Results of mechanical properties from the strand specimens were summarised in Table 3. It can be seen from Table 3 that in both series of blends prepared from the Haake batch mixer and the PTW, modulus of elasticity (E_{mod}) and tensile strength of the reactive blends are slightly higher than those of corresponding non-reactive blends. These values appear to be independent on the amount of the reactive PSU, PSU–PhA, i.e., the obtainable E_{mod} and tensile strength between Bld2 and Bld3 prepared by the PTW or between Bld5 and Bld6 prepared by the batch mixer are comparable. However,

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[1] The extrudate strand specimens yield similar stress–strain curves to the normal standard injection-moulded specimens. However, the absolute values in Emod and tensile strength of the strand specimen are about 20–30% lower than those of the normal specimens. This appears to be caused by nature and geometry of specimen themselves. However, the results from these miniature strands specimen are quite reliable and good enough for qualitative comparison in mechanical properties, when the materials are available in limited amount.

Table 3
Mechanical properties from miniature strand-specimens. Strain rate used was 5 mm/min. Average strand diameter of Bld 1–3 is 2.3 mm and of Bld 4–6 is 2.2 mm. The standard deviations reported were ± in percent

Blend	E-modulus (N/mm^2)	Tensile strength (N/mm^2)	Tensile elongation at break (%)	MVI[a] (ml/10 min)
1	2145(±8)	64(±1)	4.1(±3)	106.9
2	2330(±9)	70(±2)	23(±12)	92.4
3	2331(±5)	70(±1)	41(±18)	80.3
4	2240(±1)	46(±9)	2.4(±8)	311.3
5	2290(±4)	70(±1)	20(±13)	239.8
6	2322(±5)	70(±2)	25(±6)	149.5

[a] Melt volume index (MVI) measured at 300°C, 21.6 kg.

Table 4
Results of solvent extraction

Blend	DMF-extraction		HCOOH-extraction		Total insoluble part [wt.%]
	Soluble part [wt.%]	Insoluble part [wt.%]	Soluble part	Insoluble part [wt.%]	
1	69.0	31.0	96.2	3.8	1.22
2	67.4	32.6	62.3	37.7	12.3
3	65.7	34.3	46.1	53.9	18.5
4	68.9	31.1	99.6	0.4	0.12
5	68.1	31.9	67.2	32.8	10.5
6	67.3	32.7	46.5	53.5	17.5

an influence of PSU–PhA could be detected in terms of tensile elongation at break (ϵ_b). That is ϵ_b of the reactive systems (Blds 2, 3, 5, and 6) is much higher than those of the non-reactive systems (Blds 1 and 4). The higher content of the PSU–PhA, the higher values of ϵ_b are obtained.

From the stress–strain curve, the tensile toughness (tensile energy to break) may be estimated by integrating the area under the curve (A). As a measure of toughness improvement, A is normalised by $A_{\text{non-reactive Bld4}}$. The normalised A is plotted as a function of content of the reactive PSU, PSU–PhA as shown in Fig. 3. One sees that a remarkable improvement (15–38 times) is achieved in all reactive systems. Blends prepared by the PTW show slightly higher tensile toughness than corresponding blends prepared by the Haake batch mixer. This may partly be caused by degradation of PA chains during long mixing time in the Haake mixer. This is actually evident by the melt volume index (MVI) value shown in Table 3. The MVI of blends prepared by the batch mixer are much higher than those of blends prepared by the PTW.

Then, another interesting feature to be discussed is a morphology-toughness relationship of the blends prepared by PTW. From Fig. 1(b) and (c), it is clear that there is no significant difference in particle size between the reactive blends Bld2 and the Bld3. However, the tensile toughness of Bld3 is much larger than that of Bld2, implying that the toughness improvement in the PA/PSU system may not solely depend on the particle size of the PA dispersed phase but also on the interfacial adhesion. Actually, the effect of particle size on the mechanical properties of PA/PSU when PA is a major component as well as polystyrene/ polycarbonate blends was investigated [17,18]. It has been shown that the toughness improvement is not simply caused by the particle size reduction but by interfacial chemical bonding, i.e., without any interfacial chemical bonding, the impact toughness of the blends was hardly improved. This also may be a case here.

Cho et. al. [19] investigated the effect of maleic anhydride

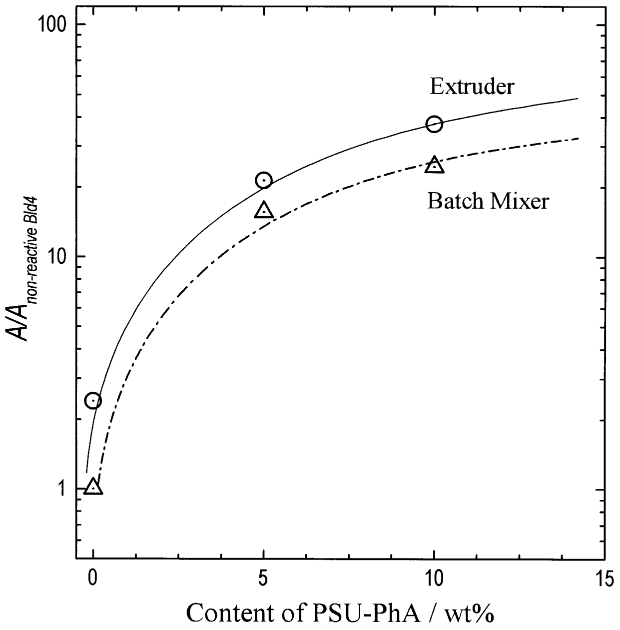

Fig. 3. Content of PSU–PhA vs the tensile toughness estimated from area under stress–strain curve of strand specimen, normalized by that of the non-reactive system Bld4 ($A/A_{\text{non-reactive Bld4}}$).

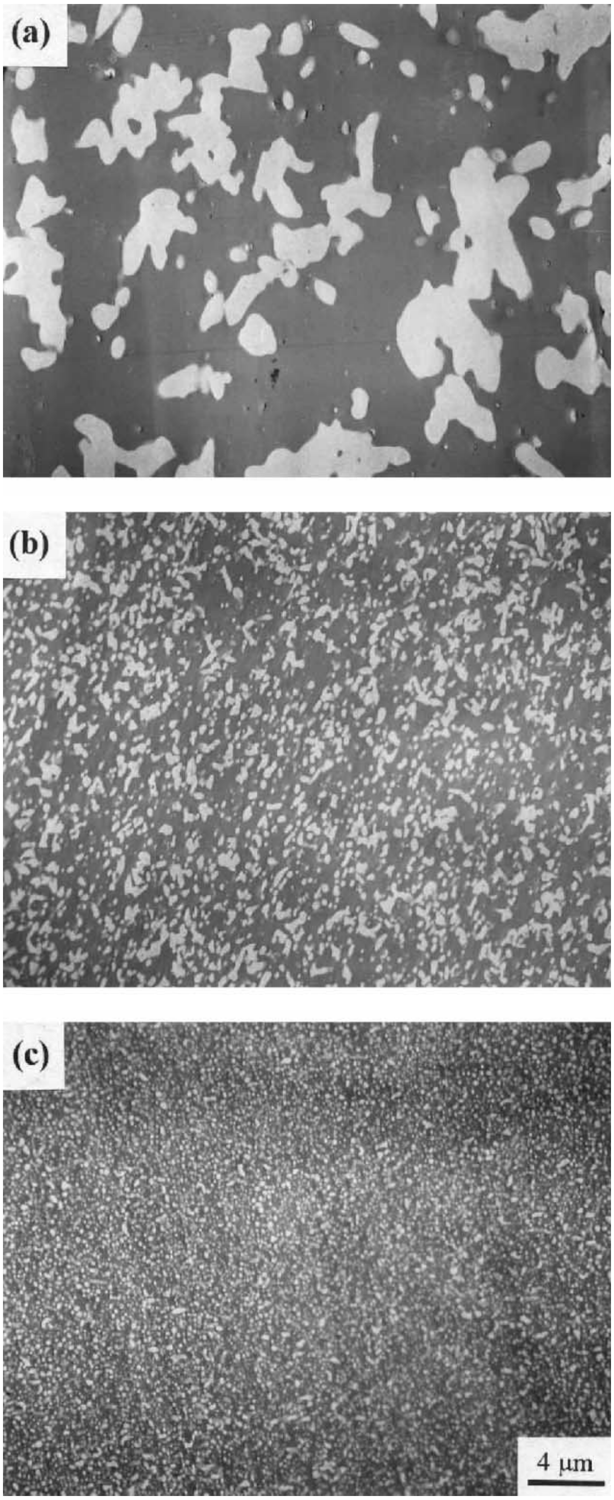

Fig. 4. TEM micrographs of the strand specimen: (a) Bld1, (b) Bld2 and (c) Bld3. Cutting direction is parallel to the flow direction.

grafted polypropylene (PP–MA) concentration on the interfacial fracture toughness evaluated by asymmetric double cantilever beam method between mixed PP and amorphous polyamide (aPA). It was reported that PP–MA gave a significant increase in interfacial adhesion. As the PP–MA concentration increases, the interfacial strength is enhanced. It follows that the enhancement of interfacial is due to the in situ formation of copolymer. The higher amount of copolymer formed at the interface, the greater interfacial strength is expected. Therefore, in our melt mixing study, it is also conceivable that amounts of in situ formed copolymer in Bld3 containing 10 wt% of added PSU–PhA would be higher than those in Bld2 with 5 wt% of added PSU–PhA. Consequently, interfacial adhesion provided by in situ formed copolymer in Bld3 would be higher than that in Bld2.

In order to provide a rough idea about the amounts of PSU–PA copolymers formed during the mixing, the solvent extraction was employed to the blends. The non-reactive PSU and PSU–PhA as a major component can be dissolved in DMF. Likewise, unreacted PA can be dissolved selectively in formic acid. The PSU–PA copolymer formed during melt mixing should not be soluble in DMF or formic acid. This fraction is an insoluble residue in the extraction procedure. The results of extraction are summarized in Table 4. In the case of non-reactive systems (Blds 1 and 4), only a small amount of insoluble residue was observed, indicating no copolymer formation has taken place. In the reactive systems, a higher amount of insoluble residue than in the non-reactive systems was detected, suggesting the formation of PSU–PA copolymer during melt blending. The more contents of loaded PSU–PhA, the higher amount of insoluble residue (higher amount of in situ formed PSU–PA copolymer) was observed. This is in reasonable agreement with the toughness results.

Fig. 4 shows TEM micrographs of the strand specimens of blends prepared by the PTW. Specimens were cut parallel to the flow direction. It can be seen that in the non-reactive system Bld1 (Fig. 4(a)), the dispersed PA phase became bigger, suggesting particle coarsening took place during the preparation process of the strand specimen in the MVI machine (preheating about 5 min and then extruding). In contrast, only small increase of the particle size of the dispersed PA during further processing of Blds. 2 and 3 was observed in Fig. 4(b) and (c). This can be correlated to the emulsifying effect of PSU–PA copolymer at the interface, to retard particle coarsening and stabilize morphology as has been mentioned.

Due to the material availability, the mechanical performance of the blends prepared by the PTW was also investigated using injection moulded ISO samples. The results

Table 5
Mechanical properties from injection molded specimens. Strain rate used was 5 mm/min

	PSU	Bld. 1	Bld. 2	Bld. 3
E-modulus (N/mm^2)	2638	2845	2945	2956
Tensile strength (N/mm^2)	80	77.6	81.2	81.4
Tensile elongation at break (%)	108	68.7	105.2	108.2
Charpy notched impact (kJ/m^2)	1.5	1.1	1.4	2.6

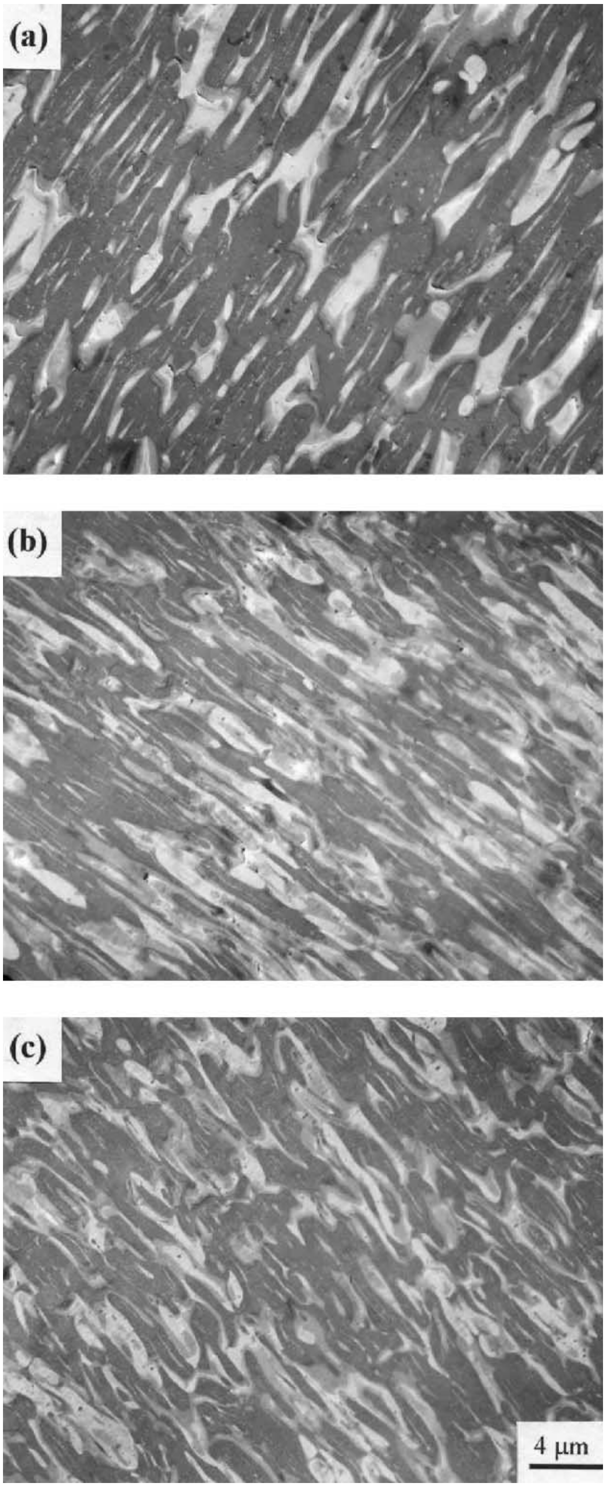

Fig. 5. TEM micrographs of the injection molded specimen: (a) Bld1, (b) Bld2 and (c) Bld3. Cutting direction is parallel to the flow direction.

are summarised in Table 5. A similar tendency as in the case of the results obtained from the strand specimens can be seen; the E_{mod} and tensile strength of the reactive blends are slightly higher than those of the non-reactive blends, while the tensile elongation at break of the reactive systems is much higher than those of the non reactive systems. Compared to pure PSU, the melt-blended PA/PSU shows quite low notched impact toughness. However, significant improvement in the notched impact was found in the Bld3, containing 10% of the PSU–PhA

In Fig. 5, TEM images of the injection-moulded specimens cut parallel to the direction of flow are shown. Surprisingly, no significant difference in morphology between the non-reactive blend (Fig. 5(a)) and the reactive blends (Fig. 5(b) and (c)) can be observed. That is all injection-moulded specimens have oriented and rather big PA particles dispersed in the PSU phase. It can be speculated that such kind of coarsened morphology may be induced by very high shear produced in the mini-injection moulding machine.[2] On the other hand, it is interesting to notice that the obtainable notched-impact toughness in the reactive system could be improved regardless the morphology. This again implies that the morphology may not be the main factor in the improvement of toughness in the PA/PSU system.

4. Conclusion

In this study, the non-reactive and reactive PSU/PA blends were prepared by the new mini-twin screw extruder and the Haake batch mixer. The morphology and mechanical properties of the blends were investigated. The study indicates that at the given processing condition, the small mini-screw extruder PTW is more effective in mixing both non-reactive and reactive PA/PSU blends than the Haake batch mixer. Therefore, the PTW is a good screening device to prepare blends of newly developed polymer or laboratory synthesized polymers, which have rather high melt viscosity and are available in limited amount.

When PSU–PA copolymers are formed in situ by the coupling reaction at the interface in the reactive systems, they act as typical emulsifiers and provide a finer particle size and better morphological stability, compared to the non-reactive system. Significant toughness improvement was found in the reactive system containing 10% of PSU–PhA. High toughness in the reactive systems appears to originate from the enhanced interfacial adhesion, not simply by the reduced particle size of PA dispersed phases. The results confirm the role of in situ formed copolymer at the interface to improve adhesion between phases.

Acknowledgements

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[2] The mini-injection-moulding machine can produce specimens starting from 150-g material and the injection volume is rather low. To produce ISO-bar specimen with good quality, the injection speed and the back-pressure must be high. The maximum shear rate is ca. 15,000 s^{-1}.

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