Macromol. Symp. **2006**, 233, 1–10 DOI: 10.1002/masy.200650101

Styrenics/Polyamide-Blends – Reactive Blending and Properties

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Summary: The combination of polyamide 6 (PA 6) and styrene-butadiene-acrylonitrile (ABS) to polymer alloys with co-continuous morphology leads to an interesting combination of properties. Using recent development in the sampling technique for Twin Screw Extruders, the morphology formation in ABS/PA 6 blends and alloys was studied by microscopy and chemical analysis. It could be shown, that the morphology of the alloys is formed in the initial phase of the extrusion step, while in the physical blend a clear correlation between the dispersion of the phases and the residence time could be observed. By chemical analysis further details of the process could be detected.

Keywords: polyamide; reactive blending; sampling techniques; styrenics

Introduction

Due to the promising combination of properties, blends of styrenics (especially Acrylonitrile-Butadiene-Styrene, ABS) and polyamides are being studied and developed for over forty years. Already in 1961, Borg-Warner commercialized ABS/PA 6-Blends under the trade name Elemid®. These materials offered good mechanical performance and compared to polyamide reduced moisture up-take.

In order to further improve the adhesion between the immiscible polymers PA and SAN (matrix of ABS), different compatibilizers were studied [2]. The most successful version of this product modification was commercialized as Triax® by Monsanto in 1987. In this product, maleic anhydride was incorporated in the SAN to form SANMA-terpolymers. These terpolymers were added to compatibilize the immiscible PA 6 and ABS [3,4]. Due to its excellent impact strength, Triax® is mainly used in automotive interior applications. Furthermore styrene-maleic anhydride-copolymers (SMA) were used to compatibilize ABS and PA 6. This approach was commercialized by DSM as Stapron® N [5]. Another approach to compatibilise ABS and PA 6 by using styrene-N-phenyl-maleinimide-maleic anhydride-terpolymers (S-N-PMI-MA) was commercialized just recently [6].

Since 1980 a large number of scientific papers, dealing with the different issues of blend formation, structure property-relationships and other issues of styrenics/polyamide blends appeared [7–12].

During the compounding of ABS/PA 6 alloys containing reactive SANMA-terpolymers, several processes are on-going within the timeframe of the extrusion process. Thus, to understand the compounding process as such and subsequently improve the process further, studies to monitor the evolution of the morphology during the extrusion process are necessary. Such investigations can be done either by using extruders which allow for a quick opening and isolation of the material for morphological studies and chemical analysis [9], or by employing recently developed

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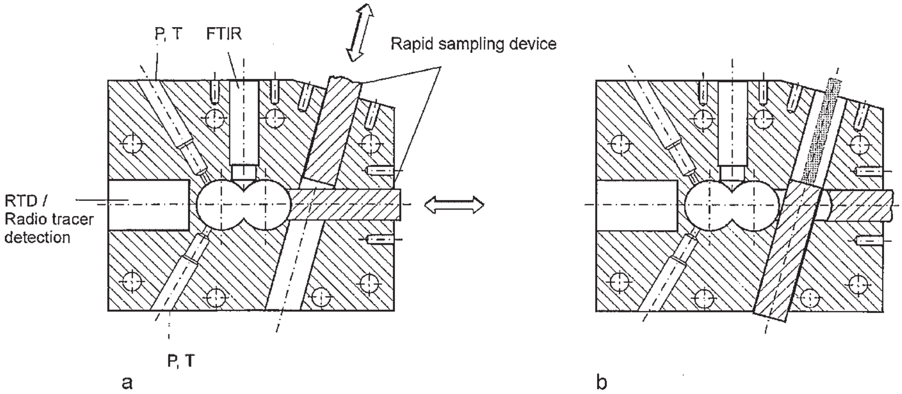

Figure 1.
Sampling device for the fast separation of melt from a Twin Screw Extruder [14].

sampling devices [13–16]. For our study, the sampling device developed by Stephan et. al. [13], according to Figure 1 was used.

The equipment shown in Figure 1 allows the separation of melt out of the barrel without interfering the extrusion process. The described sampling technologies have been widely used during the last years to study the morphology development in different blend systems, mainly PP/PA [14,17,18], PA/EPDM [19,20]. Also the grafting of maleic anhydride onto polyolefins was already studied [21].

In this paper we will summarize our efforts to study the morphology evolution in commercial ABS/PA 6-alloys during the compounding process using two different screw designs. In both cases the morphology evolution for a non-compatibilized ABS/PA 6- blend and an ABS/PA 6-alloy will be discussed.

Experimental

The employed sampling devices allow the collection of material at different zones of the extruder without interfering the process. The obtained material is quenched with liquid nitrogen to freeze the actual morphology. Subsequently the morphology is visualized by microscopy. First, the homogeneity of the samples is judged by optical microscopy, while SEM was used to obtain the detailed structure of the samples. SEM-images were taken after cross sectioning and etching the sample surface with acetone (ABS is dissolved). After that the sample surface was sputter coated with gold and images were taken using a Zeiss DSM 960 SEM. A part of the material was used for a separation procedure, according to the scheme given in Figure 2. All obtained fractions where characterised individually in order to gain information about their purity, composition and molecular weight. As ABS component Ronfalin® TZ 236, having 35 wt.-% of polybutadiene rubber was used. The polyamide 6 used had a viscosity number of 150 ml/g (0,5 wt.-%/vol. conc. H_2SO_4 at 23 °C). As SAN a product with an AN-content of 33 wt.-% was used, while the SANMA-Terpolymer had 31 wt.-% acrylonitrile and 2,1 wt.-% maleic anhydride.

The compositions of the blends are given in Table 1. For both screw designs

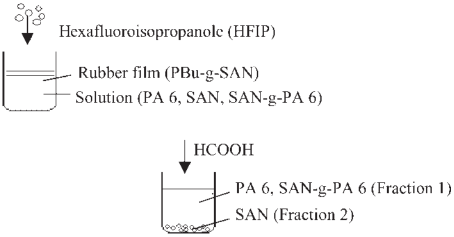

Figure 2.
Schematic representation of the extraction procedure used to separate the ABS/PA 6-alloys and blends.

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Table 1.
Compositions of the ABS/PA 6-blends.

	Composition [wt.-%]			
	ABS	PA 6	SAN	SANMA
Blend 1	54	41	5	—
Blend 2	54	41	—	5

(Figure 3) two samples were prepared using a ZSK 40 Twin Screw Extruder (Werner & Pfleiderer) at a barrel temperature of 250 °C, a screw speed of 200 rpm and a throughput of 40 kg/h.

The main difference between the two screw designs is the absence of the kneading blocks in zone 3 of screw 2). As reported in the literature [9], this might result in a finer morphology for the compatibilized material (Blend 2)

Results and Discussion

Results Obtained with Screw 1

As indicated in Figure 3, samples were taken at three positions (“PEP”). The obtained granulates were studied as well. To visualize the influence of the screw position on the morphology of each sample, SEM-images were prepared. Since the samples taken at position 1 were too brittle to be processed for microscopy, only images of the materials obtained at position 2 and 3 and for the granulate were taken (Figure 4).

From the images of blend 1, displayed on the left hand side the influence of shear on the morphology can be clearly seen. Without the compatibilizer the morphology becomes finer with increasing distance from the feeding zone. Thus increasing residence time leads to a finer morphology.

On the right hand side, the appropriate images of the blend 2, with the Terpolymer are displayed. The materials containing the compatibilizer behave completely different. At all positions the ABS distribution is much finer compared to the unmodified blend and obviously there is almost no influence between the samples taken at different positions. Already at position 2 the morphology is fixed.

This result is in line with studies regarding the impact modification of PA 6 with EPR-g-MA [19,20], where as well a very rapid reaction of the MA-units in the rubber and the PA during the first section of the compounding was observed by IR-spectroscopy.

Since the MA-content of the whole formulation is just 0,1 wt.-%, IR-spectroscopy at the crude samples will not reveal the conversion of the MA-units in the samples of Blend 2. Hence solvent extraction of the obtained materials was performed

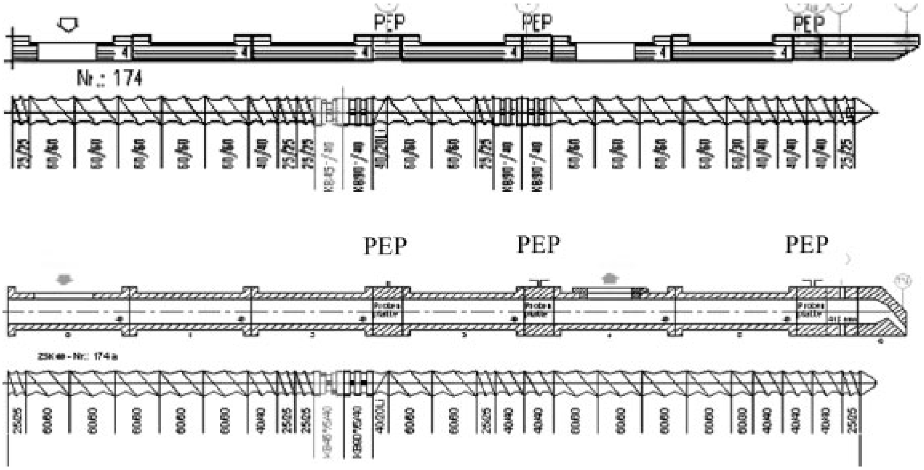

Figure 3.
Screw designs and position of the sampling plates (“PEP”).

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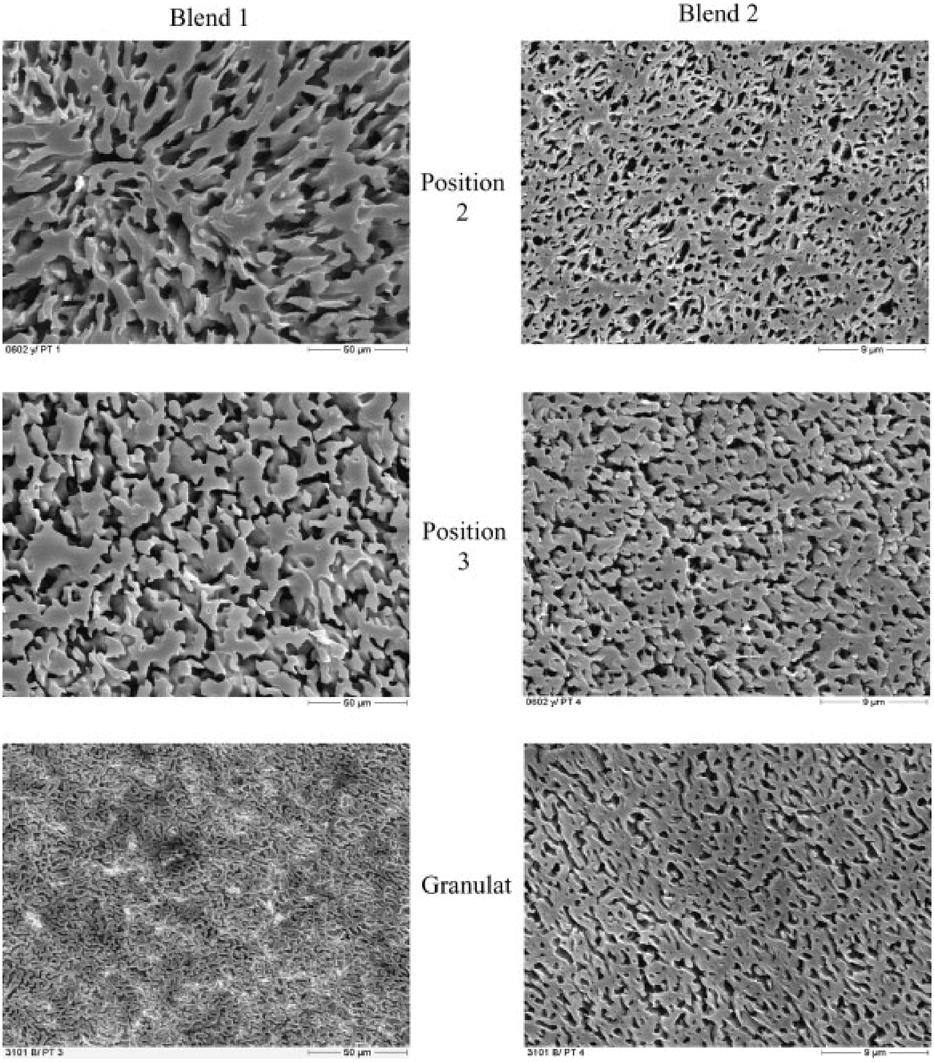

Figure 4.
SEM-images of samples of blends 1 and 2 taken at different positions (2, 3 and granulate) during the compounding with screw 1.

according to the scheme given in Figure 2. In the first separation step using 1,1,1,3,3,3-hexafluoroisopropanole (HFIP) as solvent, the matrix of the material is completely soluble, while the rubber phase of the ABS appears at the top of the polymer solution as a film. After centrifugation this top layer can be separated quantitatively from the HFIP-solution. Both fractions were dried in the vacuum and the amount of each fraction was determined. The purity and composition of each fraction was checked by DSC and IR-spectroscopy. The remaining material of the HFIP-soluble fraction is then dispersed in Formic Acid for 24 h. After this time again the non-soluble part of the fraction can be separated from the polymer solution by centrifugation.

In Table 2 the results of the extraction trials are summarized. The numbers given in brackets are the theoretical values, which are expected due to the composition of the products.

Table 2.
Composition of the blends at the different sampling positions.

	Position 1		Position 2		Position 3		Granulate	
	Blend 1	Blend 2	Blend 1	Blend 2	Blend 1	Blend 2	Blend 1	Blend 2
HFIP-insoluble (PBu-g-SAN 28,5)	28.7	33.1	29.7	35.7	28.2	35.3	30.2	35.8
SAN/SANMA (30,5)	28	26.3	28	23	29.4	22.7	28.5	23
PA6/SAN-g-PA 6 (41)	43.3	43.5	42.3	41.5	42.4	42	41.2	41.2

During the HFIP-extraction blend 1 without compatibilizer behaves different than blend 2. Within the experimental error the separated amount of PBu-g-SAN for blend 1 is almost constant for all 4 samples, and near the expected value, while the amount of non-soluble material of blend 2 is significantly higher as expected.

For the non-soluble fraction of the formic acid extraction, almost the same behaviour can be observed. In all four samples of blend 1 the same amount of material was isolated, while in blend 2 again the situation is different. A significant reduction of this fraction compared to the charged value is observed going from the feeding zone to the sample taken at position 1, as can be seen from Figure 5. A further reduction takes place from position 1 to position 2, then the amount of this fraction remains constant. Obviously a major part of the charged Terpolymer is driven to other fractions as a consequence of the chemical reaction that takes place during the extrusion process.

For the Formic Acid soluble part, no significant deviation from the expected value could be detected. In the granulates both blends show almost the charged amount of PA 6.

In order to get information about the accuracy of this separation process and further details about the chemical composition of the fractions, the individual fractions were as well characterized. For the HFIP-soluble fraction, which should mainly consist out of the PBu-g-SAN rubber, the results of the IR-spectra are summarized in Table 3.

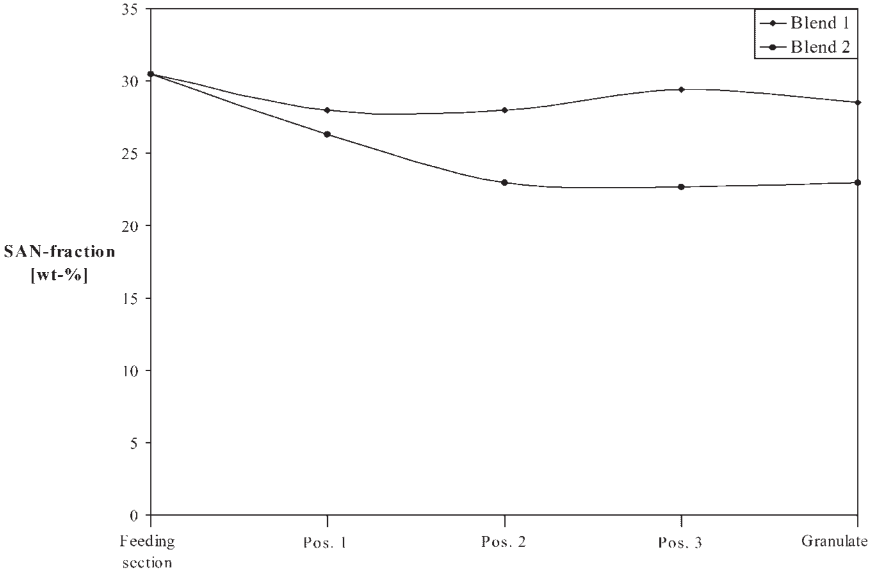

Figure 5.
Amount of the SAN/SANMA-fraction at the different screw positions for blend 1 and 2.

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Table 3.
Composition of the fractions that are not soluble in HFIP (IR-spectroscopy).

	Blend 1				Blend 2			
	Pos. 1	Pos. 2	Pos. 3	Granulate	Pos. 1	Pos. 2	Pos. 3	Granulate
PBu-g-SAN [wt.-%]	94.5	95.9	97.6	95.8	89.4	80.1	80.7	80.1
PA 6 [wt.-%]	5.5	4.1	2.4	4.2	10.6	19.9	19.3	19.9

In all samples of blend 1 a small amount of PA could be detected, while in blend 2 a large amount of PA 6 is fixed in this fraction. The results for blend 1 indicate, that no complete separation of the rubber fraction and the PA 6 could be achieved. Obviously the rubber film is contaminated by the HFIP-solution, thus small amounts of soluble material remain in this fraction. On the other hand, the amount of PA 6 incorporated in the fractions of blend 2 is far beyond the level of impurity, hence a part of the PA 6 is attached to the rubber phase or has become non-soluble in HFIP during the extrusion process. It should be noted, that the amount of fixed PA 6 in the PBu-g-SAN fractions increases in the same manner as the amount of SANMA decreases in the SAN/SANMA-fraction of blend 2.

Since a large part of the charged PA 6 is fixed in the rubber fraction it is clear, that the PA 6 fractions have to contain another material. As can be seen from the data summarized in Table 4, again a large difference between blend 1 and blend 2 can be observed.

Only a small amount of SAN is trapped in the PA-fraction, hence the separation technique works well for the non-compatibilised mixture (blend 1). The amount of trapped SAN in the different samples of blend 2 is significantly higher than in blend 1. Obviously a part of the terpolymer has reacted with the PA 6 to form the SAN-g-PA 6. This is as well corroborated by IR-spectroscopy, since for all samples of blend 2 signals of Imid-groups could be detected, while this was not the case for the samples of blend 1.

Assuming that the samples obtained from blend 2 contain also a small amount of trapped SAN (appr. 2 wt.-%), and taking the relative amount of this fraction into account, the part of SANMA, which has reacted with PA 6 and which is soluble in HFIP can be calculated. It turns out, that approximately 50% of the charged SANMA is incorporated in these fractions. Another indication for the existence of the SAN-g-PA 6 copolymers in the Formic Acid soluble part comes from the measurement of the solution viscosity. As can be seen from Figure 6, the viscosity number of the fraction obtained from blend 1 are almost constant at each position, while for blend 2 in all cases higher values were obtained. The values obtained for the different positions correlate qualitatively with the amount of fixed SANMA in the appropriate PA-fraction. From previous trials it is known, that SAN-g-PA 6 has higher viscosity numbers than PA 6.

From these trials it can be concluded, that a part of the in situ formed compatibilizer SAN-g-PA 6 remains soluble in HFIP as well as in Formic Acid, as expected and proved by comparative trials. On the other hand it is not clear at this point, why obviously a part of the SANMA or the

Table 4.
Composition of the fractions separated from different samples of blends 1 and 2 (IR-spectroscopy).

	Blend 1				Blend 2			
	Pos. 1	Pos. 2	Pos. 3	Granulate	Pos. 1	Pos. 2	Pos. 3	Granulate
PA 6 [wt.-%]	98	98.2	97.7	98.1	92.7	94.3	92.5	91.4
SAN [wt.-%]	2	1.8	2.3	1.9	7.3	5.7	7.5	8.6

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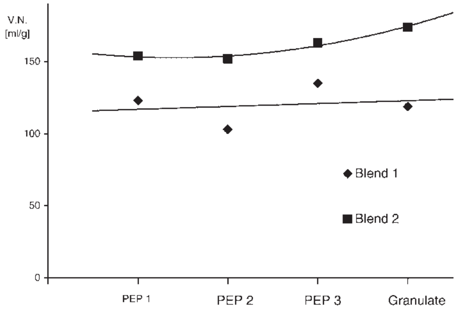

Figure 6.
Viscosity number of the PA 6/SAN-g-PA 6 fractions of the samples obtained at different positions of the extruder.

reaction product with PA 6 remains non-soluble in HFIP. The reason for this will be studied in the future.

Experiments with Screw 2

As proposed in the literature for PA 6/SAN-blends compatibilised by imidized acrylic [9], a smoother screw configuration can sometimes give smaller particle size of the dispersed phase in reactively compatibilised systems.

This might have a beneficial influence on the performance of such products. Subsequently, trials with a smoother screw configuration, where the kneading section in zone 3 is removed (Figure 2b), were run for the same blends. Again the SEM-images were taken to visualize the development of the morphology using the new screw design (Figure 7).

Again no sample could be prepared from the material obtained at position 1. For the blend 1, the sample obtained at position 2 had a very coarse morphology, while the morphology at position 3 and for the granulate are comparable with the images obtained with screw 1 (Figure 4). For the blends with the compatibilizer, the images show no significant differences compared to the samples obtained with screw design 1.

The results of the extraction trials according to the previously described method are summarized in Table 5.

The trends are similar than in the trials with screw design 1, although the scattering of the data is larger than in the previous samples. Again the most striking difference can be seen for the data of the SAN/SANMA-fractions. Obviously all charged SANMA reacts with polyamide and is driven to other fractions. In these trials the amount of SAN-g-PA 6 for blend 2, which appears in the Formic Acid soluble fraction, is significantly larger than in the previous trials.

To visualize the influence of the screw design in more detail TEM-images of the blends 2 prepared with the different screws are prepared. Ultra thin sections were stained with OsO_4 and Phosphoric Tungsten Acid (PTA) (Figure 8).

Both samples have a co-continuous morphology, but in the case of screw 1, the structure is clearly finer than in the sample obtained with screw design 2. On the other hand, within the PA-phase of the sample prepared by screw 1, much more finely dispersed SAN-particles are visible. The screw with the larger mixing power obviously creates a better dispersion of the two immiscible phases, but also a significant amount of SAN-g-PA 6 is driven away from the interface into the PA-phase, which would explain the comparatively large amount of bright spots in the PA-phase.

The granulates of the four samples were as well moulded into ISO-test bars to

Table 5.
Composition of the blends at the different sampling positions.

	Position 1		Position 2		Position 3		Granulate	
	Blend 1	Blend 2	Blend 1	Blend 2	Blend 1	Blend 2	Blend 1	Blend 2
HFIP in-soluble PBu-SAN (28,5) [wt.-%]	29.6	31.9	30	31.9	31.8	34.6	30.8	32.6
SAN/SANMA (30,5) [wt.-%]	27.8	24.2	29.3	25.6	28.8	23.8	29.6	23.3
PA 6, SAN-g-PA6 (41) [wt.-%]	42.6	43.9	40.7	42.5	40.4	41.6	39.6	44.1

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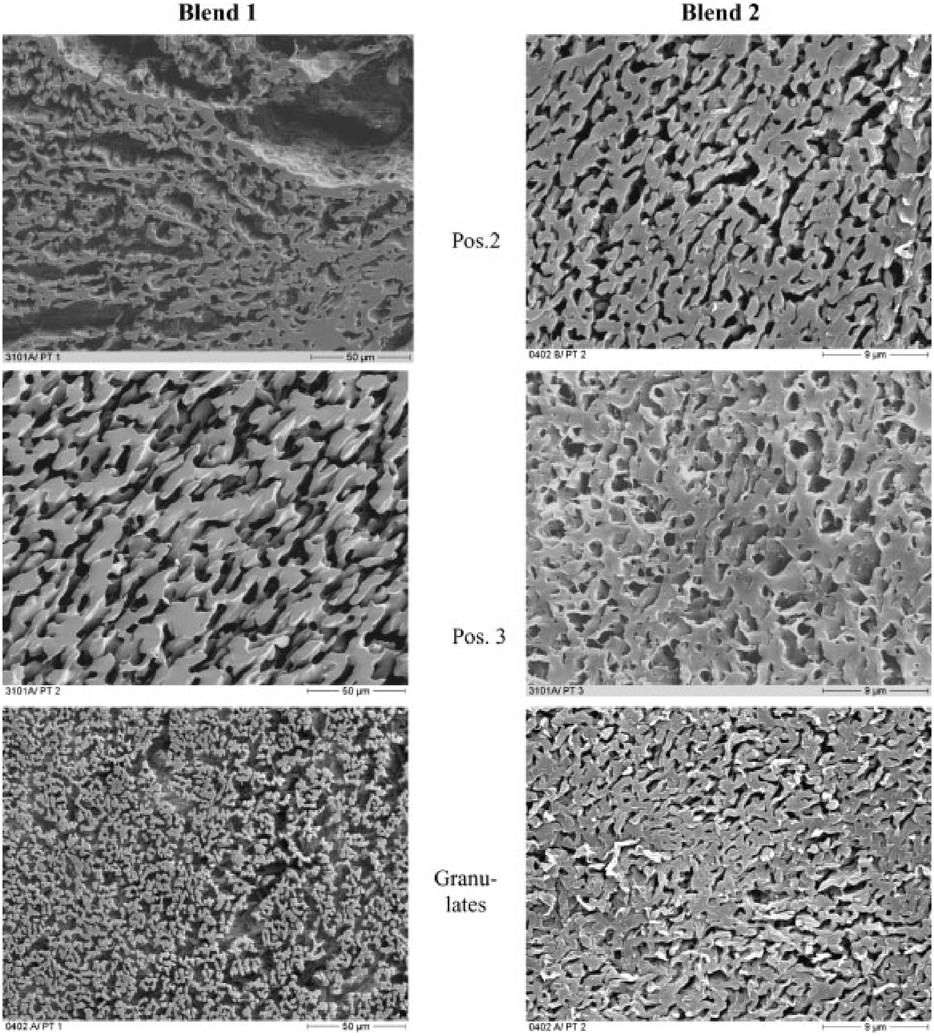

Figure 7.
SEM-images of samples from blends 1 and 2 taken at different positions (2, 3 and granulate) during the compounding with screw design 2.

determine the mechanical performance. The main results are summarized in Table 6.

The heat resistance, characterized by the Vicat B method, is identical for all four samples. The viscosity of the blends without Terpolymer is much lower than the viscosity of the compatibilized blend 2, but within the corresponding samples no influence of the screw design is visible. To characterize the toughness of the materials the Charpy notched impact and the puncture test were used. In both tests a tremendous difference between the blends 1 and blends

Table 6.
Mechanical properties of the different samples.

		Blend 1		Blend 2	
		Screw 1	Screw 2	Screw 1	Screw 2
Vicat B	[°C]	106	105	106	106
MVR	[ml/10′]	9	10	4.2	4.9
Notched Impact (“Charpy”)					
RT	[kJ/m^2]	5	5	59	66
−30 °C	[kJ/m^2]	3	4	16	18
Puncture Test					
RT	[Nm]	13	11	73	72
−30 °C	[Nm]	6	5	85	86

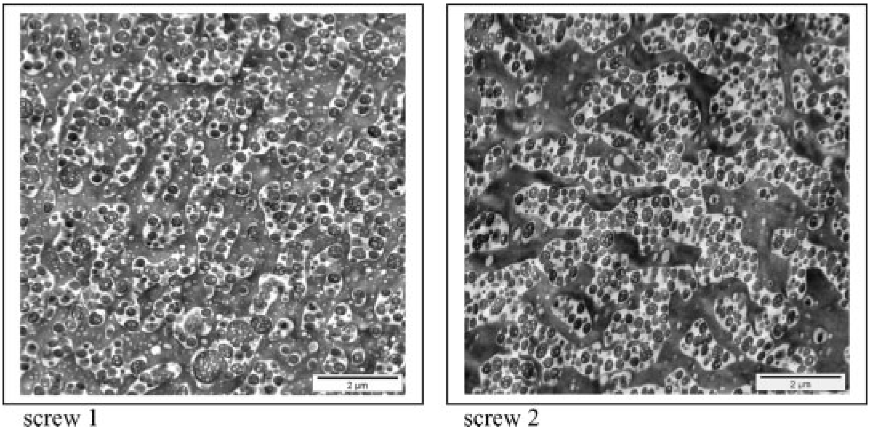

Figure 8.
TEM-images of the blends 2 prepared by different screw designs (taken at granulates, staining with OsO_4 and PTA).

2 are visible. Within the blends 2, screw 2 leads to products with slightly higher Charpy notched impact, while the results of the puncture test are identical.

The improvement of the Charpy impact at room temperature is outside the standard deviation of that method, but it does not correlate with the observed morphology, since the dispersion of the phases was better for the product compounded with screw 1. On the other hand, this result correlates with the observation of the extraction, which clearly showed that the sample compounded with screw 2 has more soluble SAN-g-PA 6. Obviously further trials are necessary to understand the complicated relation between the various parameters completely.

Conclusions

The combination of polyamide 6 (PA 6) and styrene-butadiene-acrylonitrile (ABS) to polymer alloys with co-continuous morphology leads to an interesting combination of properties. For the production of such materials, the compounding is an essential step. Using recent development in the sampling technique for Twin Screw Extruders, the morphology formation in ABS/PA 6 blends and alloys was studied by microscopy and chemical analysis. It could be shown, that the morphology of the alloys is formed in the initial phase of the extrusion step, while in the physical blend a clear correlation between the dispersion of the phases and the residence time could be observed. By chemical analysis further details of the process could be detected. The complete conversion of the SANMA already at sampling position 2 corroborated results of other groups about the very fast reaction of maleic anhydride units and amino-groups. Furthermore a significant fraction of SAN-g-PA 6, which was not soluble in HFIP, was detected. The chemical nature of this material will be studied in the future.

While the SEM-images reveal no significant difference for the alloys prepared with the different screw designs, the TEM-analysis clearly showed two significant differences. The screw with the higher mixing power gave a product with a finer dispersion of the phases but with a significant amount of dispersed SAN in the PA-phase. The SAN-particles in the PA-phase are considered to belong to SAN-g-PA 6 micelles. The influence of these two parameters on the performance of the material will be studied in the future.

Acknowledgements: The authors wish to thank B. Cunningham and D. Garau for their assistance.

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