Miscibility and Mechanical Behavior of SAN/NBR Blends

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Summary: Aiming the development of high toughness polymer materials, blends of poly(styrene-co-acrylonitrile) (SAN) and poly(butadiene-co-acrylonitrile) (NBR) rubbers, with contents of acrylonitrile (AN) varying from 21 to 45%, were prepared by casting, coprecipitation and monoscrew extrusion followed by injection molding. SAN/NBR blends, prepared in the compositions (w/w) 90/10, 80/20, 70/30, 60/40, and 50/50, were characterized by differential scanning calorimetry (DSC) and Izod impact tests. DSC analyses showed that blends with 33% AN NBR prepared by casting, and with 39% AN NBR prepared by coprecipitation, are partially miscible at 60/40, 70/30 and 80/20 (SAN/NBR) compositions and immiscible for 50/50 compositions. On the other hand, 90/10 SAN/NBR systems were totally miscible. The blends with 45% AN NBR prepared by coprecipitation showed partial miscibility to 50/50, 60/40, 70/30 and 90/10 compositions and total miscibility to 80/20 composition. The NBR addition results in a significant increase in the impact resistance, strongly dependent on the blend composition and the NBR AN content. The best result of impact resistance — 75.2 ± 8.6 ($kJ \cdot m^{-2}$) — was obtained for SAN/NBR 50/50, using 45% AN NBR. This value is 15.7 times bigger than that for pure SAN -4.8 ± 0.7 ($kJ \cdot m^{-2}$).

Keywords: blends; mechanical properties; miscibility; processing; toughening

Introduction

Blends of SAN, a stiff and brittle thermoplastic matrix, with nitrile rubber (NBR) are widely studied due to the great increase of the matrix toughness. Ahn et al.[1] and Leitzke[2] studied the miscibility and the mechanical properties of a 70/30 SAN/NBR system, varying the acrylonitrile content and the viscosity of the rubber phase and observed two different phases, one richer in NBR and other richer in SAN. Despite the fact that these blends are not totally miscible, they show a dramatic increase in the impact strength, due to the energy dissipation by the dispersed rubber particles. Cowie et al.[3] determined the segmental interaction parameters for SAN/NBR systems, verifying that most of the compositions are immiscible and that the miscibility increases with the acrylonitrile content in both copolymers.

In this work, the miscibility and the morphology of SAN/NBR systems, in a wide range of compositions and varying the acrylonitrile content of the rubber from 33 to 45%, are studied. The behavior of the blends, prepared by casting, coprecipitation or extrusion/injection molding, was evaluated by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), tensile and impact tests.

Experimental Part

The following polymers were used in the work: SANGEL LW 6827 (SAN) and Krynac 3335 C (NBR 33) (Bayer S.A); NBR 3960 (NBR 39) and NBR 4560

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Table 1.
Characteristics of copolymers used in this study.

Copolymer	% acrylonitrile	Mooney viscosity	T_g
	w/w	$1 + 4$ (100 °C)	°C
SAN	32	-	109
Krynac 3335C	32.7	33	-28
NBR 3960	39	50	-16.6
NBR 4560	45	58	-9.6

Table 2.
DSC data from SAN/NBR 33 films.

Blend Composition SAN/NBR 33	T_g			
% w/w	°C			
50/50	-33.5			110.3
60/40	-29.4			107.2
70/30	-33.5	5.1		108.8
80/20	-28.1	0.2	84.8	107.6
90/10	-4.2			94.9

(NBR 45) (Petroflex). The details are given in Table 1. Solutions of the copolymers were prepared in tetrahydrofuran (THF) and mixed in the following proportions (SAN/NBR, w/w): 100/0, 90/10, 80/20, 70/30, 60/40, 50/50 and 0/100. Films were prepared by casting on a glass plate and dried in a vacuum oven at 50 °C for 48 h. Coprecipitates were prepared by adding the solutions in methanol. Films and coprecipitates were analyzed by DSC in a 2920 MDSC calorimeter (TA Instruments), at 10 °C $\cdot$ min^{-1} under nitrogen, and by SEM on a DSM 940 A (Zeiss) microscope at 10 kV. The same compositions were also prepared by extrusion followed by injection molding. The specimens, after conditioned according to ASTM 618, were submitted to tensile tests in an EMIC testing machine (ISO-527) at a constant cross-speed of 50 mm $\cdot$ min^{-1}. The tensile properties were determined using five samples for each composition. The impact strength properties of specimens were determined using 10 samples for each composition with a microtest testing machine (ISO 180—Izod impact test). The impact fracture surfaces were also analyzed by SEM.

Results and Discussion

Table 2 summarizes the DSC data for casted films of SAN/NBR 33 systems. It is observed that 50/50 and 60/40 blends are immiscible, presenting two glass transition temperatures (T_gs) corresponding to the pure copolymers. 70/30 blends show an additional T_gs at approx. 5 °C, that corresponds to a new NBR-rich phase (76% NBR, following Fox equation), while 80/20 systems presents two additional T_gs, one richer in NBR (0.22 °C) and another one richer in SAN (ca. 85 °C). 90/10 blends show two T_gs far from those of the pure copolymers.

Table 3 and 4 show the T_gs observed from DSC analyses of SAN/NBR 39 casted films (Table 3) and coprecipitates (Table 4). These systems are partially miscible for all blend compositions, as the T_g of SAN is shifted to lower temperatures. An additional T_g appears in several SAN/NBR 39 systems. It is also observed that the blend preparation method had no influence on the DSC behavior of these systems.

The T_gs of DSC analyses from SAN/NBR 45 coprecipitates are listed in Table 5. All compositions formed partially miscible systems, as inferred by the shift of the T_gs of the pure copolymers and the presence of additional T_gs.

Figure 1 shows a SEM micrograph of a 70/30 SAN/NBR33 blend prepared by casting. It is observed nearly spherical elastomeric domains with sub-inclusions of SAN.

On the other hand, a SEM micrograph of a 70/30 SAN/NBR39 blend prepared by coprecipitation shows a dual semicontinuous morphology, as shown in Figure 2.

Table 3.
DSC data from SAN/NBR 39 films.

Blend Composition SAN/NBR 39	T_g			
% w/w	°C			
50/50	-14.3			87.9
60/40	-14.9		80.3	97.3
70/30	-14.9	7.5		90.1
80/20	-17.2			93.3
90/10	-2.0			99.0

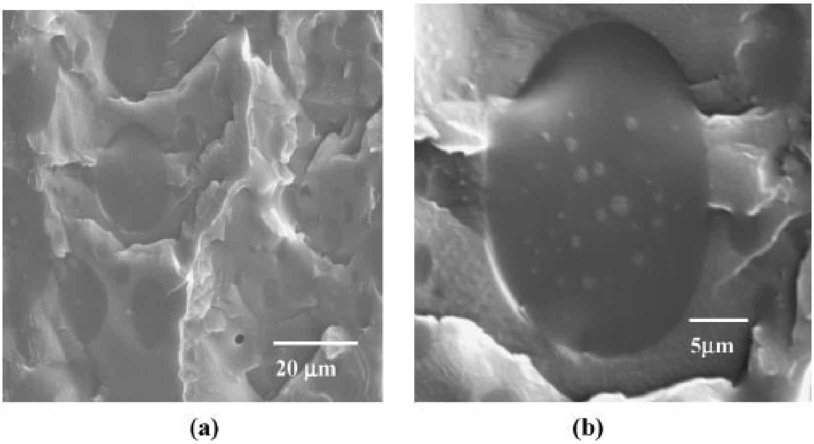

Figure 1.
SEM micrographs of 70/30 SAN/NBR33 blend prepared by casting: (a) 1 000×, (b) 3 000×.

Mechanical tests of injection molded specimens show that the addition of NBR results in a significant increase in the impact resistance, strongly dependent on blend composition and the NBR AN content (Figure 3). The best result of impact resistance—75.2 ± 8.6 (kJ $\cdot$ m^{-2}) —was obtained for SAN/NBR 50/50, using 45% AN NBR. This value is 15.7 times bigger than that for pure SAN—4.8 ± 0.7 (kJ $\cdot$ m^{-2}).

Table 4.
DSC data from SAN/NBR 39 coprecipitates.

Blend Composition SAN/NBR 39	T_g			
% w/w	°C			
50/50	−12.7			88.2
60/40	−15.9		73.8	97.2
70/30	−25.7	3.7		93.1
80/20	−10.0			96.6
90/10		7.9		95.3

Table 5.
DSC data from SAN/NBR 45 coprecipitates.

Blend Composition SAN/NBR 45	T_g		
% w/w	°C		
50/50	−3.7		110.6
60/40	−4.8		99.8
70/30		3.5	99.5
80/20	−10.1		83.6
90/10	−3.3	7.6	97.7

On the other hand, the modulus and the tensile strength are greatly decreased when the NBR content is higher than 30% w/w (Figure 4).

SEM analyses of the fracture surfaces of specimens submitted to impact tests show that cavitation and plastic deformation processes are also related to the blend composition and the NBR AN content (Figure 5). Rubber-rich blends with lower NBR AN contents lead to the development of cavitation and plastic deformation and better impact strength.

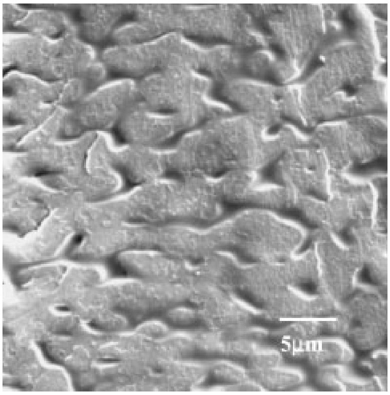

Figure 2.
SEM micrograph of 70/30 SAN/NBR39 blend prepared by coprecipitation. Magnification: 3 000×.

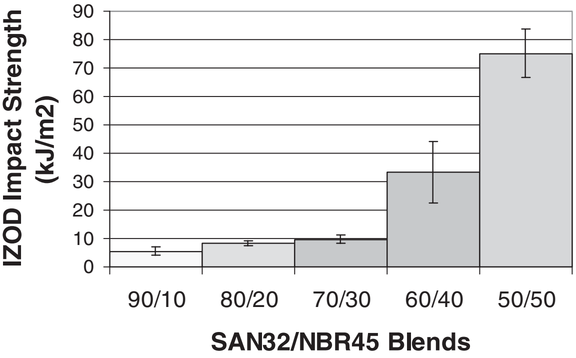

Figure 3.
The influence of NBR content on the impact behavior of SAN32/NBR45 blends.

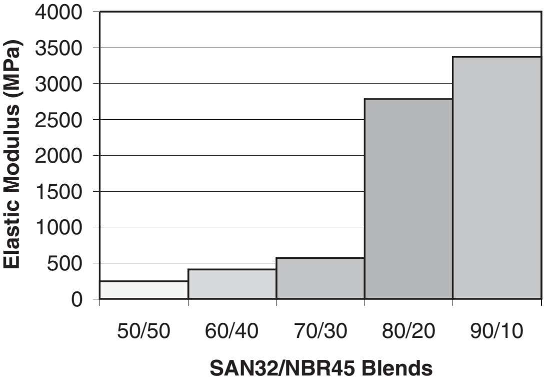

Figure 4.
The influence of NBR content on the tensile modulus of SAN32/NBR45 blends.

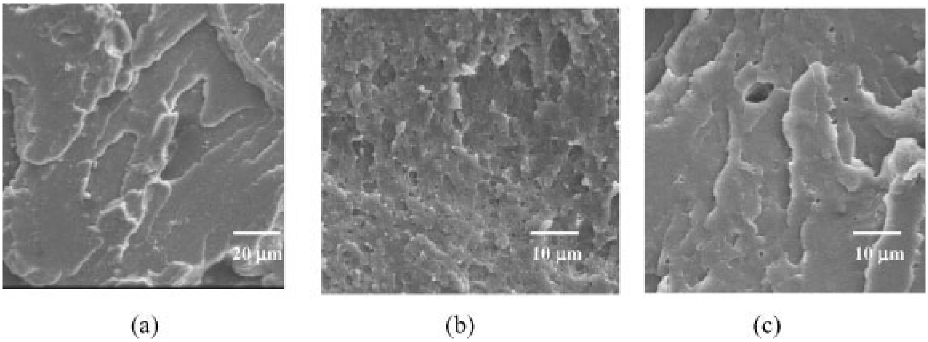

Figure 5.
SEM micrographs of impact fracture surfaces of injection molded SAN/NBR blends: (a) 90/10 SAN32/NBR45, 500×; (b) 70/30 SAN32/NBR33, 1 000×; (c) 70/30 SAN32/NBR45, 1 000×.

Conclusion

It was observed that systems with SAN contents higher than 60% are partially miscible, independent of the preparation method. It is also observed the formation of NBR-rich and SAN-rich phases.

On the other hand, the morphology of the blends depends on the preparation method. For blends prepared by casting it was observed a discrete distribution of nearly spherical elastomeric domains with SAN sub-inclusions, while the coprecipitates showed a dual semicontinuous morphology. This fact is probably related to the kinetics of the blend formation. The slow solvent evaporation favors a nucleation and growth mechanism, while the rapid coprecipitation induces a semicontinuous blend.

The mechanical behavior of SAN/NBR systems is strongly dependent on the blend composition and the NBR AN content. Higher NBR content results in a significant increase in the impact resistance, but the tensile modulus is decreased.

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