PMMA/SAN and SAN/PBT nanoblends obtained by blending extrusion using thermodynamics and microrheology basis

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Abstract. Styrene-Acrylonitrile (SAN) copolymer has been blended to poly(methyl methacrylate) (PMMA) and to poly(butylene terephthalate) (PBT) to obtain polymer nanoblends based on thermodynamics and microrheological aspects. PMMA/SAN and SAN/PBT blends show miscibility windows for a specific range of acrylonitrile (AN) content in the SAN copolymer. The phase diagram for both blends has been calculated using the interaction energy density parameter B as function of AN content in the SAN. A critical interaction energy density parameter, B_{crit} , was also calculated to find the miscibility window for both SAN blends. For some of the used SAN in the blends it was possible to obtain nanoblends as the AN content would allow B values close to the B_{crit} . For immiscible PMMA/SAN and SAN/PBT blends the disperse particle size was predicted using suitable equations and it was observed by transmission electron microscopy (TEM). Acrylic copolymers were used as compatibilizer to modify the interfacial tension and reduce the disperse phase dimensions. The compatibilizer has shown strong effect by reducing the interfacial tension and by preventing the coalescence effect. The compatibilized blends have shown disperse particle size within the nanoscale.

Keywords: nanomaterials, polymer blends and alloys, nanoblends, compatibilization

1. Introduction

Nanostructured polymer blends are polymeric systems in which the dispersed-phase domains exhibit length scales of 100 nm or less. Usually those polymer blends are referred to as nanoblends [1]. Although, the same terminology can be found in the literature to describe mixture of inorganic nanoparticles with polymer, which should mostly be referred as nanocomposites [2]. Nanoblends have been developed to be applied in electronic, membrane, sensing probes and optical applications [3–5]. There are several approaches to obtain nanoblends. Reactive extrusion has been used to produce nanostructured polymer blends based on polyamides [1]. *In situ* blend

polymerization has also been used to develop several kind of nanoblends [6, 7]. Solution casting blending has been preferred to obtain nanoblends for those systems with poor thermo-mechanical stability to be prepared by melt mixing [8, 9]. The most used method to prepare nanoblends is by melt blending [10, 11]. Polymer nanoblends can be designed by two approaches, one considering thermodynamics aspects and the other one considering microrheology basis [12]. The interaction energy density parameter (B) can be used to predict polymer blends phase separation with disperse domains in the nanoscale, as proposed by Paul and Bucknall [13]. B parameter is strictly related to the Flory-Huggins

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interaction parameter χ and depends on the polymers solubility parameters δ_i . There is a critical B value (B_{crit}) for any polymer blend which is calculated according to Equation (1):

$$B_{\text{crit}} = \frac{RT}{2} \left(\sqrt{\frac{\rho_A}{(\bar{M}_w)_A}} + \sqrt{\frac{\rho_B}{(\bar{M}_w)_B}} \right)^2 \quad (1)$$

where, ρ_A , ρ_B and $(\bar{M}_w)_A$, $(\bar{M}_w)_B$ represent densities and the weight average molecular weights of polymers A and B , respectively. In addition, R and T represent gas constant and absolute temperature, respectively. For those blends whose B value is lower than B_{crit} the final state of mixing is miscible. On the other hand, those which B is larger than B_{crit} the final mixing states are immiscible. In addition, when B is larger than B_{crit} , but the difference among them is small, the disperse particle size may become small enough to reach nanoscale. By choosing adequate polymer pairs it is possible to vary B values below and above B_{crit} to obtain miscible and immiscible polymer blends. Poly(methyl methacrylate)/styrene-acrylonitrile copolymer blends, PMMA/SAN, have been studied because it allows to have miscible and immiscible blends depending on the acrylonitrile (AN) content in the SAN [14–16]. There is an AN content limit in the SAN above which PMMA/SAN blends become immiscible with disperse phase in the range of nanoparticles. That is referred to as miscibility copolymer composition window. Paul and Barlow [17] have shown how to find the miscibility window for copolymer blends using a binary interaction model based in the interaction energy density parameter B . Miscibility windows for PMMA/SAN have been set for SAN copolymer containing from 9 to 35 wt% of acrylonitrile (AN) [18], depending on the SAN molecular weight. Higashida *et al.* [19] have shown the same trend for PMMA/SAN blends basing on Flory-Huggins parameter χ , however by increasing temperature of PMMA/SAN miscible blend it was possible to have a lower critical solution temperature (LCST). Shimomai *et al.* [20] have used the equation of state theory to show the PMMA/SAN miscibility window and have also predicted a LCST by increasing temperature. By changing the AN content in the SAN copolymer the B interaction parameter of the PMMA/SAN blend can be increased just above the B_{crit} value reaching an immiscible state. However, the disperse phase may show nanoscale domains size which allow to obtain nanoblends. This is one of the objectives of the present paper.

As described in the paper nanostructured blends or nanoblends can be obtained by choosing the interaction energy density parameter B just above the critical B value (B_{crit}). That approach is based on the Thermodynamics of a homopolymer and a copolymer mixture. On the other hand, when B for any polymer blend is well above the B_{crit} , nanostructured blends can be obtained by choosing adequate micro-rheological parameters for the blend such as: disperse and matrix phases viscosity ratio; shear and extensional flow conditions and interfacial tension or energy. All those parameters affect the final particle size of the blend disperse phase. In addition, sometimes compatibilization is necessary to reduce the interfacial tension and to prevent the coalescence for higher disperse phase content in the polymer blend [21]. One of main rheological parameters is the viscosity ratio between the liquids, which can be determined by Equation (2) [22]:

$$\eta_r = \frac{\eta_d}{\eta_m} \quad (2)$$

where η_d and η_m are the viscosity values for the disperse and matrix phase at the mixing temperature, respectively. For simple shear flow at small Newtonian liquid deformations, the particle diameter D , due the drop breakup, can be determined by balancing interfacial tension (Γ) and shear forces ($\dot{\gamma}\eta_m$), as shown in Equation (3):

$$D = \frac{4\Gamma(\eta_r + 1)}{\dot{\gamma}\eta_m \left(\frac{19}{4}\eta_r + 4 \right)} \quad (3)$$

where $\dot{\gamma}$ is the shear rate and η_m is the matrix phase viscosity. The above equation is valid for $\eta_r < 2.5$. Wu [23] has modified it to represent drop breakup in polymer blends. Thus the previous equation becomes Equation (4):

$$D = \frac{4\Gamma(\eta_r)^{\pm 0.84}}{\dot{\gamma}\eta_m} \quad (4)$$

where 0.84 is a empirical exponent and the plus (+) sign applies for $\eta_r > 1$, while minus (–) sign applies to $\eta_r < 1$. Equation (4) is applied to compositions lower than 15 wt% of the disperse phase and $\dot{\gamma}$ close to 100 s^{-1} . In addition, Sundararaj and Macosko [22] have extended it to include viscoelastic effects during the polymeric drop breakup. It was established a critical capillary number value, C_{acrit} , above which drop breakup for polymer blends will occur leading

to disperse particle diameter size D , estimated by Equation (5):

$$D > \frac{2\Gamma C_{\text{acrit}}}{(\eta_m \dot{\gamma} - N_1)} \quad (5)$$

where, N_1 represents the first normal stress difference due to the elastic forces during polymer mixing. C_{acrit} can be estimated as approximately 0.5 for $0.1 < \eta_r < 1$. By optimizing shear and extensional flow conditions, as well as, reducing as much as possible the interfacial energy, Γ , it is possible to obtain disperse particle size in the range of nano-scale. In addition, it is necessary to prevent as much as possible the particles coalescence, which can be done through compatibilization and for lower contents of the disperse phase component. Li and Shimizu [10] have obtained nanoblends from poly(vinylidene fluoride) (PVDF) by melt mixing. Polyamide 11 (PA11) particle size in the range of 20 to 100 nm was obtained at very high shear. Similar morphology was obtained for acrylic rubber (ACM) in PVDF blends [24]. Lumlong *et al.* [25] have obtained very small disperse particles for poly(butylene terephthalate)/SAN blends, PBT/SAN, under certain shear conditions and for lower disperse phase content.

The main contribution of this work is to obtain nanoblends by choosing either adequate thermodynamics parameters such as the interaction energy density parameter B or adequate microrheological parameters such as viscosity ratio and interfacial energy. The latter one can be reached by using compatibilizers. There are few works about nanoblends in the

literature obtained from melt mixing and none using that approach.

2. Experimental

2.1 Materials

PMMA was supplied by UNIGEL, Brazil, as Acrigel® DHLEP, SAN copolymer samples were supplied by BASF, Brazil, as LURAN® 358N and 388S, PBT was supplied by SABIC Innovative Plastics, Brazil, as Valox® 325. Table 1 shows the properties of the materials used in this study. An acrylic compatibilizer based on methyl methacrylate (MMA), glycidyl methacrylate (GMA) and ethyl acrylate (EA) comonomers was synthesized through bulk copolymerization at 60°C for 1 hour. MMA was supplied by Sheet Cril, Brazil, while GMA and EA were supplied by Sigma-Aldrich, Brazil. Azobisisobutyronitrile (AIBN), used as initiator, was by DuPont Brazil as Vazo® 64. MMA comonomer was previously distilled under vacuum. The acrylic copolymer, referred as MGE, was obtained with the composition MMA 88 wt%, GMA 10 wt% and EA 2 wt%, as used by Hale *et al.* [26]. EA comonomer was mainly used in the copolymer as a stabilizer to prevent molecular unzipping scissions. Two MGE samples were synthesized to give low and higher molecular weight samples, MGE 1 and MGE 2 respectively. Table 1 shows the main characteristics of all materials used in this study.

2.2. Processing conditions

All polymer blends were prepared by melt mixing using a co-rotated intermeshing twin screw 19 mm

Table 1. Characteristics of the materials used in this study.

Materials	MFI [g/10 min] ^a	$\bar{M}_n$ [g/mole] ^b	$\bar{M}_w$ [g/mole] ^b	$\frac{\bar{M}_w}{\bar{M}_n}$	AN [%] ^c	[COOH] [meq/(K·g)] ^f
PMMA	4.6	75 670	113 350	1.5	–	–
SAN 24 (LURAN 358N)	7.5	107 440	156 860	1.5	24	–
SAN 31 (LURAN 388S)	2.6	166 050	321 200	1.9	31	–
PBT (Valox 325)	14.0	39 175 ^c	45 000 ^d	–	–	45.3
MGE 1	–	13 950	81 810	5.9	–	–
MGE 2	–	26 370	102 720	3.9	–	–

^aASTM D1238: 230°C and 3.8 kg;

^bGPC: THF and 40°C;

^cViscosimetry: Borman method [27];

^dBased on polycondensation molecular weight polydispersity index;

^eElementar analysis;

^fTitration: Pohl method [28]

diameter extruder from B&P Process Equipment and Systems, U.S.A., model MP19, with L/D as 25. All materials were previously dried under vacuum at 60°C. The PMMA/SAN blends were melt blended in the extruder using a temperature profile from 180 to 220°C and 170 rpm as screw speed, while the SAN/PBT blends were mixed from 220 to 240°C at 140 rpm and 200 rpm. Both polymer blends were dried for 12 hours at 60°C before to be injection molded as testing specimens. The temperature profile for the injection molding was from 210 to 240°C. Table 2 shows all the prepared PMMA/SAN and SAN/PBT blends compositions.

2.3 Characterization

The blends morphology was observed by transmission electron microscope (TEM), PHILIPS, model CM120, Oregon. All samples were ultracryomicrotomed at -60°C with section thickness in the range of 30 to 50 nm. The sections of both kinds of blends were stained by ruthenium tetroxide, RuO_4 , vapor. All the micrographs taken from the TEM had their particle size analysis made by Image-Pro Plus. At least 300 particles were considered in the image analysis of each sample. For the PMMA/SAN blends the average particle size and its distribution were obtained using equivalent diameter particle size and considering the projected disperse phase area. On the other hand, for SAN/PBT blends ellipses were considered to measure the shorter axis (B). In addition, the equivalent diameter was also calculated from the particles projected area (D_n).

Shear viscosity data for the studied materials was obtained by capillary rheometry using an INSTRON capillary rheometer, model 4467, Massachusetts, U.S.A. All the viscosity measurements were done at 240°C, using a capillary die with 33 as L/D . The shear rate was swept from 100 to 30 000 s^{-1} . The interfacial tension data used for SAN 24/PBT blends were obtained from parallel plate rheometry. Viscosity values were obtained under rotational and oscillatory conditions as a function of shear rates and frequency. An ARES rheometer from Rheometric Scientific, model strain control, U.S.A., was

used with a 25 mm parallel plate diameter, with shear rate in the range of 0.01 to 100 s^{-1} and oscillatory frequency in the range of 0.01 to 500 rads/s. The distance between plates was fixed as 6 mm and the strain amplitude was set in the linear viscoelastic range. All measurements were done at 240°C under dry inert nitrogen gas flow.

3. Results and discussion

Considering the PMMA/SAN and SAN/PBT blends, the interaction energy density parameter B was calculated as a function of the AN content in the SAN using Equation (6) for each one and plotted as function of AN content in Figure 1. The B_{crit} value, calculated from Equation (1), was also plotted in Figure 1 to show the miscibility windows for SAN blends. Parameter B for a homopolymer 1 (PMMA or PBT)/copolymer 2-3 (copolymer S-AN) blend can be calculated by Equation (6):

$$B = B_{12}\phi'_2 + B_{13}\phi'_3 - B_{23}\phi'_2\phi'_3 \quad (6)$$

where B_{12} represents the interaction between monomer from homopolymer 1 and comonomer 2 from copolymer 2-3. In the same way B_{13} represents interaction between monomer from homopolymer 1 and comonomer 3 from copolymer 2-3. B_{23} represents the interaction between the comonomers from copolymer 2-3. On the other hand, ϕ'_2 and ϕ'_3 represent the comonomer volume fraction contents 2 and 3 of the copolymer 2-3, respectively. For the PMMA/SAN blends B_{12} and B_{13} are represented by the interaction parameters $B_{\text{MMA-S}}$ and $B_{\text{MMA-AN}}$, respectively, while B_{23} is represented by $B_{\text{S-AN}}$. For SAN/PBT blends B_{12} and B_{13} are represented by the interaction parameters $B_{\text{PBT-S}}$ and $B_{\text{PBT-AN}}$, respectively, while B_{23} is represented by $B_{\text{S-AN}}$. The B_{ij} values for each interaction pair are shown in Table 3. On the other hand, ϕ'_2 and ϕ'_3 represents the weight fraction content of styrene (S) and of acrylonitrile (AN) comonomers in the SAN copolymer. Calculations were done considering volume fraction close to the weight fraction because all components density is quite close to 1 g/cm^3 .

Table 2. Polymer blends formulations prepared by extrusion and injection molded

Materials	PMMA/SAN 24 [wt%/wt%]	PMMA/SAN 24/MGE 1 [wt%/wt%/wt%]	SAN 24/PBT [wt%/wt%]	SAN 24/PBT/MGE 2 [wt%/wt%/wt%]
SAN 24	[99/1]; [97/3]; [95/5]; [90/10]	[94/1/5]; [92/3/5]; [90/5/5]; [85/10/5]	[90/10]	[94.5/3/2.5]; [90.9/5/4.1]; [81.8/10/8.2]
SAN 31	[99/1]; [97/3]; [95/5]; [90/10]	[94/1/5]; [92/3/5]; [90/5/5]; [85/10/5]		

Table 3. Binary interaction energy density B_{ij} for styrene (S), acrylonitrile (AN), methyl methacrylate (MMA) and poly(butylene terephthalate) (PBT) pair combinations estimated at 200°C for PMMA/SAN blends and at 240°C for SAN/PBT blends [29]

Pairs ij	B_{ij} [cal/cm ³]
S-AN (200°C)	7.00
S-MMA	0.26
MMA-AN	4.45
S-PBT	0.51
AN-PBT	7.40
S-AN (240°C)	6.86

Table 4 shows the B_{crit} values for both PMMA/SAN blends, calculated using Equation (1). The interceptions of those values with the B parameter curve, as shown in Figure 1, determines the range of AN content in the SAN copolymer for the miscibility window. For the PMMA/SAN blend the range of the miscibility window is set from 13.0 up to 27.1 AN wt%, while for the SAN/PBT blend the miscibility window stays between 17.8 and 21.9 AN wt%. Considering SAN 24 and SAN 31 as copolymer components in the PMMA/SAN blends, according to the miscibility window, PMMA/SAN 24 is miscible while PMMA/SAN 31 is immiscible. On the other hand, using SAN 24 as copolymer component in the SAN/PBT blends, those blends are immiscible. In addition, for PMMA/SAN 31 the B value, 0.0619 cal/cm³, is close to the B_{crit} , 0.0090 cal/cm³, from which it might be expected to obtain PMMA/SAN nanoblends, as proposed by Paul and Bucknall [13]. The same expectation can be extended to the SAN 24/

Figure 1. Interaction energy density parameter B for the PMMA/SAN and SAN/PBT blends as function of acrylonitrile (AN) content in the SAN copolymer. B_{crit} , calculated by Equation (1), has been plotted as dash straight lines to show the miscibility window for both blends.**Table 4.** Critical interaction energy density parameter (B_{crit}) for both PMMA/SAN and SAN/PBT blends calculated at 200°C and 240°C, respectively

SAN blends	B_{crit} [cal/cm ³]
PMMA/SAN 24	0.0111 ^a
PMMA/SAN 31	0.0090 ^a
SAN 24/PBT	0.0277 ^b

^aValues calculated for the PMMA and SAN densities at 200°C^bSAN and PBT densities at 240°C

PBT blends in which the B value, 0.0351 cal/cm³, is even closer to its B_{crit} , 0.0277 cal/cm³.

Figure 2 shows the TEM morphologies for PMMA/SAN 24 miscible blend. It can be observed that PMMA/SAN 24 blend stays quite as a homogeneous single phase, thereby representing a miscible blend. The RuO₄ interacts strongly with the aromatic rings from the styrene comonomer of SAN. Therefore, the dark spots observed in the images are assigned to the SAN copolymer. Figure 3 shows PMMA/SAN 31 blends TEM micrographs at different compositions. Phase separation can be observed for the PMMA/SAN 31 blends, where the dark domains are SAN 31 RuO₄ stained particles. All morphological observations seem to agree with the phase behavior which has been predicted by the thermodynamics analysis from Figure 1. Most of the SAN 31 disperse particles has size below 100 nm,

Figure 2. TEM micrographs obtained for PMMA/SAN 24 blend 90/10, as injection molded

Figure 3. PMMA/SAN 31 blend TEM micrographs and particle size distribution histograms at different compositions, as injection molded: (a) 99/1; (b) 97/3; (c) 90/10

as shown in Figure 3. PMMA/SAN 31 nanoblends were mainly obtained for lower SAN 31 contents as can be observed from the respective particle size distribution histograms of the PMMA/SAN 31 nanoblend, as shown in Figure 3. At lower SAN 31 contents most of its particles are below 100 nm. The SAN 31 particle average size, obtained from the histograms in Figure 3, is shown in Table 5. As proposed by Paul and Bucknall [13] the parameter energy density $B_{\text{PMMA/SAN 31}}$ is small enough, compared to the B_{crit} , that very small particles can be obtained within the nanoscale size. As previously cited, the PMMA/SAN blends were prepared by melt mixing and injection molded. Most of the thermodynamics applied to analyze polymer-polymer miscibility is based on the mixing state equilibrium. On the other hand, polymer blending obtained by melt extrusion is well far away from the thermody-

namics equilibrium due to the unstable temperature and pressure. Therefore it is surprising that the predicted thermodynamic conditions to produce nanoblends can be applied within the melt blending conditions and still obtains nanoparticles as expected. Even so, the PMMA/SAN 31 blend morphology gives results as been in the equilibrium state of mixing, at least for lower SAN 31 contents. As the amount of SAN 31 is increased in the blend, the coalescence mechanism becomes more pronounceable leading to less stable mixing, as predicted by Tokita [30].

The blend viscosity ratio can be obtained for PMMA/SAN and SAN/PBT blends from capillary rheometry, as shown in Figure 4. All blend components have a strong pseudoplastic behavior. According to Equation (2) the viscosity ratio η_r can be calculated for any shear rate for all studied blends in this work. The PMMA matrix viscosity and the SAN 31/PMMA viscosity ratio can be observed in Table 6 for several shear rates. That viscosity ratio is close to 1. As consequence a good SAN 31 dispersion in the PMMA matrix would be expected. According to Equation (4) the particle diameter D would only depends on the interfacial tension and the rheological forces. As the shear rate increases the rheologi-

Table 5. SAN 31 disperse phase average particle size for the PMMA/SAN 31 blends, as injection molded

PMMA/SAN 31	Average equivalent diameter [nm]	Standard deviation [nm]
99/1	63	± 14
97/3	77	± 20
90/10	181	± 48

Figure 4. Apparent viscosity curves obtained from capillary rheometry for PMMA, SAN 24, SAN 31, PBT and PBT+MGE 2 measured at 240°C

Table 6. Capillary viscosity for PMMA, SAN and viscosity ratio for their blends

Shear rate [s ⁻¹]	Shear viscosity [Pa·s]		Viscosity ratio $\frac{\eta_{SAN}}{\eta_{PMMA}}$	Rheological force, $\dot{\gamma}\eta_m$ [Pa]
	PMMA	SAN 31		
100	196	240	1.22	19 600
200	142	164	1.15	28 400
300	112	126	1.13	33 600
500	83	92	1.11	41 500
1000	58	63	1.09	58 000
2000	38	40	1.05	76 000
5000	21	22	1.04	105 000

cal force increases, which would reduce. The interfacial tension ν_{12} can be calculated by the harmonic average equation (Equation (7)) [31]:

$$\nu_{12} = \nu_1 + \nu_2 - \frac{4\nu_1^d\nu_2^d}{\nu_1^d + \nu_2^d} - \frac{4\nu_1^p\nu_2^p}{\nu_1^p + \nu_2^p} \quad (7)$$

where ν_1 and ν_2 are the surface tension, while ν_1^d and ν_2^d are the non-polar surface tension components and ν_1^p and ν_2^p are the polar surface tension for components 1 and 2 of the blend, respectively. The surface tensions ν_i for PMMA and SAN 31 at 20°C was obtained from Wu [23] and extrapolated for 220°C according to Ito *et al.* [32]. Both values are 24.4 and 25.1 mN/m, respectively. The polar surface tensions ν_i^p were calculated for PMMA and SAN 31 by Equation (8) as 6.85 and 2.87 mN/m, respectively:

$$\nu_i^p = X_i^p \nu_i \quad (8)$$

where X_i^p is the polarity for both components, which are 0.280 and 0.110 for PMMA and SAN 31,

respectively. The ν_i^d is obtained as $(1 - \nu_i^p)$ and it is 17.53 mN/m for PMMA and 23.23 mN/m for SAN 31. As result, ν_{12} can be calculated as 1.3 mN/m for the PMMA/SAN 31 blend. On the other hand, the PMMA/SAN 31 viscosity ratio can be chosen as 1.09 at shear rate close to 1000 s⁻¹, because the used range of shear rates where the PMMA/SAN melt blending was prepared has been calculated for the twin screw extruder running at 170 rpm [33]. Thus, the minimum shear rate occurs in the conveying screw section at 51 s⁻¹, while the maximum shear rate is in the kneading screw section which is 1127 s⁻¹. Considering that most of the particle breaking occurs between the kneading elements, the particle size can be estimated from Equation (4) by using the power index as +0.84. Thus the particle size D was estimated as 96.8 nm, which is within the values of D shown in Table 5. However, the estimated D through Equation (4) has not included viscoelastic effects on the drop breaking.

MGE 1 copolymer was used to modify the interfacial tension for PMMA/SAN 31 blends. Figure 5 shows the blend morphology for the ternary PMMA/SAN 31/MGE 1 blends.

The interface has changed from a sharp transition to a white halo around the SAN disperse phase, as indicated by the black arrows in the micrographs, which can be considered as an interphase. That interfacial region is certainly a MGE rich phase because it cannot be stained by RuO₄. MGE 1 has no aromatic ring in its chemical structure to be stained by RuO₄. The presence of MGE 1 has prevented the coalescence effect because it has allowed a reduction in the SAN 31 average particle size as shown in Figure 6. The SAN particle size has shown a significant reduction mainly for higher contents where the coalescence is more effective to increase the particle size. As result all SAN 31 contents have shown the average particle size in the nanoscale range. Gan and Paul [34] has predicted phase separation for SAN/MGE blends at temperatures above 185°C, when SAN has 32.3 wt% of AN and MGE has between 8 and 14 wt% of GMA. Therefore it could be expected that MGE 1, containing 10 wt% of GMA, would be immiscible with SAN 31 at temperatures above 185°C. In addition, the blending temperature in the extruder was around 220°C and the injection molding temperature was 240°C. Both temperatures are well above 185°C established by the

Figure 5. TEM micrographs for melt mixed PMMA/SAN 31/MGE 1 blends, injection molded at 240°C: (a) 94/1/5; (b) 92/3/5

Figure 6. SAN 31 average particle size (D_n) as function of SAN 31 content in the PMMA/SAN 31 binary and ternary blends with MGE 1, for injection molded samples at 240°C

previous authors. Therefore, it might be expected to observe an immiscible SAN 31/ MGE 1 blend.

SAN 24/PBT nanoblends were obtained by melt mixing and injection molded, as result the TEM micrographs are shown in Figure 7. However, it was necessary to use MGE 2 as compatibilizer to reduce the PBT phase average particle size as shown in Figure 7b. MGE 2 copolymer is a reactive compatibilizer which has epoxy functional groups to react *in situ* mainly with COOH end groups from PBT molecules during the melt mixing. The grafted PBT-

MGE molecules have segments which interact with both SAN 24 and PBT phases in the SAN 24/PBT blends and may diffuse to the interfacial region, thereby reducing its interfacial energy [26]. The average particle size for the SAN 24/PBT 90/10 blends obtained from the histograms in Figure 7a is 160 ± 67 nm, while addition of MGE 2 has reduce it to 101 ± 45 nm, obtained from Figure 7b. MGE 2 has shown a good efficiency to decrease the interfacial tension for the SAN 24/PBT blend, as well as, to prevent coalescence between the disperse particles. The reduction of the interfacial energy due to the presence of MGE 2 is expected to decrease the particle size as predicted by Equation (4). The evaluation of the interfacial tension for SAN 24/PBT blends was done from its viscoelastic properties, such as, dynamic modulus and relaxation time spectrum, obtained through dynamic rotational rheometry. The SAN 24/PBT blends interfacial tension is shown in Table 7 using two different models, Choi and Schowalter [35] and Palierne [36], respectively. A significant decrease in the interfacial tension can be observed by using the reactive compatibilizer MGE 2 in the SAN 24/PBT blends. That occurs when both methods are used to obtain it, as well as, both model to estimate it. That may be one of the reasons for the reduction in the disperse phase parti-

Figure 7. TEM micrographs and particle size distribution histograms for melt mixed SAN 24/PBT/MGE 2 blends, as extruded: (a) 90/10/0; (b) 81.8/10/8.2

Table 7. SAN/PBT blends interfacial energy measured by rotational rheometry

Blends	Interfacial energy based on G' [mN/m]		Interfacial energy based on G^* [mN/m]	
	Choi	Palierne	Choi	Palierne
SAN 24/PBT (90/10)	2.36	3.26	4.72	6.51
SAN 24/PBT/MGE (88.1/10/8.2)	1.60	1.66	1.47	1.52

G' : dynamic shear modulus;
 G^* : complex shear modulus

cle size in those blends. However, the coalescence effect can occur simultaneously with the reduction in interfacial tension which can leave to an increase in particle size. On the other hand, as the amount of PBT phase is decreased in the SAN 24/PBT/MGE 2

blends there is lower probability for the occurrence of coalescence.

Figure 8 shows evidences of the coalescence prevention as PBT content is reduced in the SAN 24/PBT blends. The average particle size drops to values lower than 100 nm. The average particle size for lower PBT disperse phase content was 68 ± 27 and 91 ± 37 nm, respectively, as observed in Figure 8a and 8b. For those SAN 24/PBT compositions it was possible to obtain blends with smaller disperse particle size within the nanoscale. Coalescence effect depends basically on two parameters: number of particle collisions and the ability of a matrix film between two disperse particles to be drained out. The number of particle collisions is proportional to the square of disperse phase content and inversely

Figure 8. TEM micrographs and particle size distribution histograms for melt mixed SAN 24/PBT/MGE 2 blends, as extruded: (a) 94.5/3/2.5; (b) 90.9/5/4.1

proportional to the particle size, while the ability to drain out depends on the interfacial tension and it is inversely proportional to the matrix viscosity [37]. For lower interfacial tension values and viscosity ratio between disperse phase and matrix there is less chance to the matrix film between particles to be drained and as consequence there is coalescence suppression. From Figure 5 it is possible estimate the viscosity ratio n_r for SAN 24/PBT blends. For very low shear rates the PBT viscosity is smaller than SAN 24 viscosity. As the shear rate is increased to higher values PBT viscosity becomes closer to the SAN 24 viscosity. For very high shear rate PBT has higher viscosity than SAN 24. On the other hand, the SAN/(PBT+MGE) viscosity is higher than SAN 24 viscosity at any shear rate. Both SAN 24/PBT and SAN 24/(PBT/MGE 2) blends were melt mixed in

the twin screw extruder at 140 and 200 rpm. The lowest shear rate for both screw speed were calculated in the conveying screw section as 43 and 60 s^{-1} , respectively. On the other hand, the maximum shear rates were calculated as 930 to 1330 s^{-1} , respectively, in the kneading blocks screw sections [33]. Considering that drop breaking mostly occurs in the kneading blocks screw sections with higher shear rates, the viscosity ratio is close to 1 for the SAN 24/PBT blend and is 1.8 for the SAN 24/(PBT+MGE 2), as observed in Table 8.

According to Equation (4) the PBT particle size D can be estimated as shown in Table 9, where several values for D were calculated for different shear rates and for interfacial tension obtained by different models from Table 7. The estimated particle size for tension for Palierne model and an increase in the

Table 8. Capillary viscosity for SAN, PBT and PBT/MGE and viscosity ratio for their blends

Shear rate [s ⁻¹]	Capillary viscosity [Pa·s]			Viscosity ratio	
	SAN 24	PBT	PBT+MGE 2	$\frac{\eta_{\text{PBT}}}{\eta_{\text{SAN 24}}}$	$\frac{\eta_{\text{PBT+MGE 2}}}{\eta_{\text{SAN 24}}}$
43	999	388	1607	0.4	1.6
60	755	327	1229	0.4	1.6
930	80	82	144	1.0	1.8
1330	60	68	109	1.1	1.8

Table 9. PBT and PBT+MGE particle size estimated at different shear rates and interfacial tensions for SAN 24/PBT and SAN 24/(PBT+MGE 2) blends and obtained from TEM

Shear rate [s ⁻¹]	Shear stress, $\dot{\gamma}\eta_m$ [Pa]	Viscosity ratio		Estimated particle size, D [nm]			
		$\frac{\text{PBT}}{\text{SAN 24}}$	$\frac{(\text{PBT} + \text{MGE 2})}{\text{SAN 24}}$	PBT Disperse phase		(PBT+MGE 2) Disperse phase	
				Choi ^a	Palierne ^a	Choi ^a	Palierne ^a
930	74 400	1.0	1.8	127	177	141	146
1330	79 800	1.1	1.8	128	179	132	140
SAN 24, PBT and (PBT+MGE 2) Blends composition				Average particle size [nm] Measured from TEM			
[wt%/wt%]		[rpm]		B ^b	D _n ^b	B ^b	D _n ^b
SAN 24/PBT (90/10)		200		160±67	227±99	–	
SAN 24/(PBT/MGE 2) (94.5/3/2.5)		200		–		68±27	104±42
SAN 24/(PBT/MGE 2) (90.9/5/4.2)		200		–		91±37	111±42
SAN 24/(PBT/MGE 2) (90.9/5/4.2)		140		–		58±20	86±31
SAN 24/(PBT/MGE 2) (81.8/10/8.2)		200		–		101±45	124±45

^aThe interfacial tension values used in the calculations of *D* for PBT and (PBT+MGE 2) disperse phases were 2.4 and 1.6 mN/m for Choi model and 3.3 and 1.7 mN/m for Palierne model, respectively.

^b*B* was measured as the smaller axis of the elliptical shape of most of the disperse particles. *D_n* was calculated as the equivalent average diameter of the particles based on their areas.

viscosity ratio for higher shear rates, as observed in Table 8. The reduction in the particle size by using the Palierne model for compatibilized blends is due to the strong reduction in interfacial tension which overcomes an increase in the viscosity ratio by considering Equation (4). On the other hand, the reduction in the interfacial tension for the compatibilized blends using Choi model it was not enough to allow enough reduction in the estimated particle size, as shown in Table 9. For all estimated values no one has shown particle size below 100 nm.

The particle dimensions measured for the SAN 24/PBT blends are well above the ones for SAN 24/(PBT+MGE 2). By considering the smaller dimension *B* any of the SAN 24 blends most of them has shown average values lower than 100 nm within the range of nano particles. Although, the average equiv-

alent diameter *D_n* has shown values above 100 nm for most compatibilized blends their dimension are smaller than the estimated ones. One of the main reasons to show *D_n* lower than predicted one is that the component (PBT+MGE 2) has reduced the possibility to occur coalescence within the evaluated shear rates. The estimation done by Equation (4) does not take in account the coalescence effect. The grafted PBT-g-MGE molecules besides reducing the interfacial tension have hindered the coalescence among the disperse phase particles.

4. Conclusions

Nanostructured polymer blends based on SAN copolymers have been obtained. The window of miscibility was obtained for both PMMA/SAN and SAN/PBT blends. For PMMA/SAN blends the range

of AN content to have miscible blends has been found between 13 and 27.1 wt%, while for SAN/PBT blends the range was found between 17.8 and 21.9 AN wt%. By chosen SAN copolymers containing AN just above the window upper limit it was possible to obtain Immiscible blends. SAN copolymer with 24 AN wt% was chosen for PMMA/SAN immiscible blends, while a SAN with 31 AN wt% was chosen for SAN/PBT as well as immiscible blends. The disperse phase particle size was estimated for those blends using Wu equation. The experimentally measured particle size was found within the range of the estimated values. The use of acrylic compatibilizers has helped to obtain particle size within the nanoscale by strongly reducing interfacial tension.

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