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PMMA-AES Blends Prepared by *in situ* Polymerization

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Summary: Blends of poly(methyl methacrylate) (PMMA) and poly(acrylonitrile-*g*-(ethylene-*co*-propylene-*co*-diene)-*g*-styrene) (AES) were prepared by *in situ* polymerization. AES, a commercial elastomer obtained by radical copolymerization of styrene and acrylonitrile in the presence of ethylene-propylene-diene terpolymer (EPDM), was dissolved in methyl methacrylate and the *in situ* polymerization was conducted at 60 °C. The blends were characterized by CHN analysis, infrared spectroscopy (FTIR), carbon-13 nuclear magnetic resonance (^{13}C NMR), dynamic mechanical analysis (DMA) and transmission electron microscopy (TEM). These blends are immiscible and present complex phase behavior. Selective extraction of the blends' components showed that a fraction of the material is crosslinked and grafting reactions on EPDM chains take place during MMA polymerization. Syndiotactic PMMA was obtained in the presence of AES and this syndiotactic-specificity increased with increasing amount of AES. The morphology of polymerized specimens showed irregular domains of elastomeric phase and in some cases inclusions of PMMA could be observed.

Keywords: AES; blends; elastomers; *in situ* polymerization; PMMA

Introduction

Polymer blending provides an efficient route to develop new materials with enhanced characteristics regarding optical, chemical or mechanical performances[1,2] and owing to strong economic incentives, modification of existing materials by blending is becoming one of the attractive routes to improve properties and to generate versatile polymeric products.[3] For instance, the mechanical properties of a given polymer can be greatly modified, either improved or worsened, by incorporating particles of a second minority phase. The quality of the morphology (size, continuity, homogeneity, orientation) is crucial for the final performances of these heterogeneous materials. The most used industrial process is the incorporation of an elastomeric component in thermoplastics,[3] which alters the stress distribution in the matrix and contributes to control of a crack's propagation and termination.

Most polymer blend research has focused on materials prepared by conventional mixing of component polymers; the *in situ* formation of polymer blends via the polymerization of a monomer within a polymeric matrix has occasionally been explored.[3] *In situ* polymerization of precursor compounds (or monomers) in the presence of polymeric materials is an important preparation method allowing precise design of material properties and simplicity in processing. Polymer blends prepared through *in situ* polymerization may possess morphologies that result from reaction-induced phase separation, and thus provide the final products with superior properties in comparison with materials prepared with other techniques. The development of complex morphologies in these blends during the polymerization has been observed to significantly improve the ultimate properties such as impact strength.[4] The most commercially significant example of *in situ* blend formation is found in the

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toughening of polymers by rubber modification.[5] The essential characteristic of rubber toughening is that the impact resistance of the parent rigid polymer increases substantially, in return for a limited reduction in stiffness.[6] High-impact polystyrene (HIPS) is one of the more important toughened polymers in which brittle polystyrene becomes more ductile.[7]

Poly(methyl methacrylate) (PMMA) is a glassy amorphous polymer with excellent optical properties, which is extensively used in manufacturing industries because of its high resistance to ultraviolet degradation and corrosion.[8] However, PMMA has the disadvantage of poor impact toughness, which makes it unsuitable for many engineering purposes. The most common method for promoting the toughness of PMMA is blending with elastomers. A suitable choice of particle size and chemical composition can lead to substantial improvements in crack and impact resistance, without significantly compromising the optical properties,[9] because the rubbery phase acts as a stress concentrator and craze initiator.[3] The toughening of PMMA has been investigated by many authors.[10,11] Poomalai *et al.* [3] prepared blends of PMMA with poly(ethylene-*co*-vinyl acetate) (EVA) by melt blending and observed enhancements of 67% in the impact resistance of PMMA/EVA (20 vol% of rubber). Cheng and Chen[12] prepared PMMA/EVA blends by *in situ* polymerization of MMA in the presence of the rubber and the Izod impact strength of the PMMA/EVA blends increased 320% after incorporation of 10 wt% EVA. The differences in the mechanical properties of the blends prepared by both research groups [3,12] basically reflect the special morphology developed during *in situ* polymerization and also the possibility of a grafting reaction between the polymeric components. The results reported in these papers show how powerful the method of *in situ* polymerization is for improving the properties of blends.

Poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) and high impact polystyrene (HIPS) are important commercial polymers, which present low thermal resistance and low weatherability due to the high level of unsaturation of its rubber phase.[13,14] This limitation can be overcome by using saturated elastomers like ethylene-propylene-diene terpolymer (EPDM) instead of polybutadiene. For this purpose, the polymer poly(acrylonitrile-*g*-(ethylene-*co*-propylene-*co*-diene)-*g*-styrene) (AES), is very attractive due to having an impact strength comparable to ABS and better environmental and thermal resistance.[13] AES is a thermoplastic elastomer constituted of free EPDM, free poly(styrene-*co*-acrylonitrile) (SAN), and a graft copolymer of SAN on EPDM chains. In this system, the graft copolymer EPDM-*g*-SAN molecules act as compatibilizers between SAN and EPDM phases. Turchet[15] prepared PMMA/AES blends by mechanical mixing and obtained a toughened blend with 30 wt% of AES. This blend exhibited an increase of 990% in impact resistance, in comparison with PMMA, and this result is due to SAN compatibilizing effect, improving adhesion and dispersion of EPDM particles in the PMMA matrix.

In this work PMMA-AES blends were prepared by *in situ* polymerization of methyl methacrylate monomer in the presence of AES. The advantages of the *in situ* polymerization are the possibility of the reaction between PMMA chains and AES, increasing the compatibility between these components.

Experimental Part

Materials

Crompton Corporation supplied AES (Royaltuf® 372P20). AES is a complex mixture of SAN, EPDM and grafted copolymer EPDM-*g*-SAN. AES contains 13 wt% of free EPDM, 22 wt% of free SAN and approximately 65 wt% of EPDM-*g*-SAN. The SAN presents 27 wt% of acrylonitrile content. The global composition of AES is 50 wt% of SAN and 50 wt% of EPDM. The EPDM of AES contains

68.9 wt% of ethylene, 26.5 wt% of propylene and 4.6 wt% of 2-ethylidene-5-norbornene (ENB) as diene.[16]

Methyl methacrylate monomer (Proquigel Química S/A) was submitted to extraction of polymerization inhibitors with a 5% NaOH solution. After this, the organic layer was washed with distilled water. Then MMA monomer was dried using Na_2SO_4 and distilled at 25 °C under vacuum. Methyl methacrylate monomer was stored at −15 °C.

In situ Polymerization of PMMA-AES Blends

AES was dissolved in chloroform (1:6 w/v) under stirring during 1 h at room temperature. Then methyl methacrylate monomer was added and the mixture was stirred during 48 h before the polymerization. Benzoyl peroxide (0.1 wt%) was added to the viscous and homogeneous solution and the polymerization was carried out at 60 °C for 192 h. Each polymerization reaction produced approximately 550 g of material. Methyl methacrylate monomer and chloroform residue were extracted at 120 °C in a vacuum oven for 48 h. Poly(methyl methacrylate) homopolymer was also prepared at 60 °C under similar conditions. Table 1 presents the composition of the PMMA-AES blends expressed in terms of AES content (wt%). The AES content in the blends was calculated from the nitrogen percentage determinated by elemental analysis. The nomenclature used to describe the blends is based on the EPDM content. For example, the blend containing 6.9 wt% of EPDM is named 6.9EPDM.

Selective Extraction of the Blend Components

The components of the PMMA-AES blends were continuously extracted using a Soxhlet apparatus. First, the EPDM phase was extracted with hexane (named Fraction 01), followed by simultaneous extraction of the PMMA, SAN, EPDM-*g*-SAN with chloroform (named Fraction 02). Each extraction step was performed for 72 h. The residue of the extraction was named insoluble phase. This procedure was performed in duplicate.

Fourier Transformed Infrared Spectroscopy (FTIR)

Films of these three fractions were compression molded in a Marconi MA 098/A Hydraulic Press at 180 °C with 10-ton press and characterized by infrared spectroscopy.

Attenuated total reflection spectra of the films of extracted phase were collected using an Illuminat IR (Smiths Detection) equipped with a ZnSe internal reflection element (45°). A spectral range of 4000–650 cm^{-1} was used with 64 scans collected per spectrum and a resolution of 4 cm^{-1}.

Carbon-13 Nuclear Magnetic Resonance (^{13}C NMR)

The tacticity of poly(methyl methacrylate) in the blends was determined by ^{13}C NMR spectra obtained using an Inova 500 spectrometer operated at 125 MHz at room temperature on $CDCl_3$ solutions using 10 mm tubes. The sample concentration was 10% (w/v). Nuclear Overhauser enhancement in the ^{13}C NMR spectra was suppressed by inverse gated decou-

Table 1.
PMMA-AES blends prepared in this work.

Name	EPDM in MMA solution (wt%)[a]	EPDM in the blend (wt%)[b]
3EPDM	1.5	3
3.3EPDM	3	3.3
5.9EPDM	4.5	5.9
6.9EPDM	6	6.9
7.9EPDM	7.5	7.9

[a] EPDM content in MMA solution before polymerization.
[b] EPDM content in blends calculated from elemental analysis.

pling. The pulse angle used was 45°, acquisition time was 1 s, the interval between was pulses 10 s and the spectral width was 35000 Hz.

Dynamic Mechanical Analysis (DMA)

Blend specimens ($9.0 \times 6.0 \times 1.0$ mm) were submitted to sinusoidal deformation at a frequency of 1.0 Hz and amplitude of 0.02% in the temperature range from -100 to 210 °C, at a heating rate of 2 °C/min, in a Rheometric Scientific DMTA V Analyzer.

Transmission Electron Microscopy (TEM)

Blend morphologies were studied using a Carl Zeiss CEM 902 transmission electron microscope. The films were ultramicrotomed under cryogenic conditions (-140 °C) to obtain ultrathin sections (40 nm). Phase contrast between the blend components was achieved by exposing the samples to vapors of OsO_4 for a period of 4 h.

Results and Discussion

In the present work, PMMA-AES blends were prepared by *in situ* polymerization of methyl methacrylate using chloroform as solvent. The initial AES/chloroform/methyl methacrylate solution is transparent, and this is evidence that the solution is homogeneous. After polymerization and extraction of the residual monomers and solvent the PMMA-AES blends are still optically clear, suggesting that the blends are miscible or the phase dimensions in the heterogeneous mixture are lower than the wavelength of visible light. The miscibility window for PMMA with SAN has been reported in the literature[17] and it depends on the molar mass of the polymers, on the temperature and on the acrylonitrile content in the SAN. The blends are totally miscible when the weight fraction of acrylonitrile units in SAN copolymer is within the interval between 9% and 33%.[5,18] Feng *et al.*[19] studied the miscibility between PMMA and SAN using ^{13}C NMR, suggesting that the miscibility in this system is due to attractive interactions between the carbonyl group of PMMA and the phenyl group of SAN copolymer. Kwei *et al.*[20] also concluded that miscibility between PMMA and SAN involves interaction between the carbonyl group of PMMA and phenyl group of SAN, based on IR absorption measurements.

Selective Extraction of the Blends Components

The structure of the blends can be better understood using selective extraction methodology with characterization of each fraction. The EPDM phase can be extracted with hexane, which is a nonsolvent for PMMA and SAN. PMMA and SAN are soluble in the same solvents making this separation impossible.

Table 2 shows the weight percentage of each fraction. The insoluble phase increases with AES content, varying from 4.5% (for 3EPDM) to 19.2% (for 7.9EPDM). These results suggest that crosslinking takes place during the polymerization of methyl methacrylate monomer in presence of AES.

During polymerization secondary reactions can occur, resulting in crosslinking of the EPDM macroradical (Figure 1). The complex sequence of free radical reactions is initiated by the thermal decomposition of the peroxide into two oxy radicals, which can further decompose *via* β-scission. The crosslinking occurs *via* H-abstraction from the rubber chain by the radicals formed upon peroxide decomposition, followed combination or addition of EPDM macroradicals.[21]

Table 2.
Percentage of each extracted phase of PMMA-AES blends.

Materials	Percentage of extracted phase (%)		
	Fraction 01	Fraction 02	Insoluble phase
3EPDM	– *	93.9 ± 0.5	4.5 ± 0.7
3.3EPDM	– *	92.6 ± 0.2	5.7 ± 0.2
5.9EPDM	0.9 ± 0.2	88.2 ± 0.3	9.3 ± 0.2
6.9EPDM	1.2 ± 0.4	80.6 ± 0.2	16.1 ± 0.5
7.9EPDM	1.5 ± 0.6	77.6 ± 0.4	19.2 ± 0.4

*The extraction the EPDM content in these blends was not possible because the EPDM content is low.

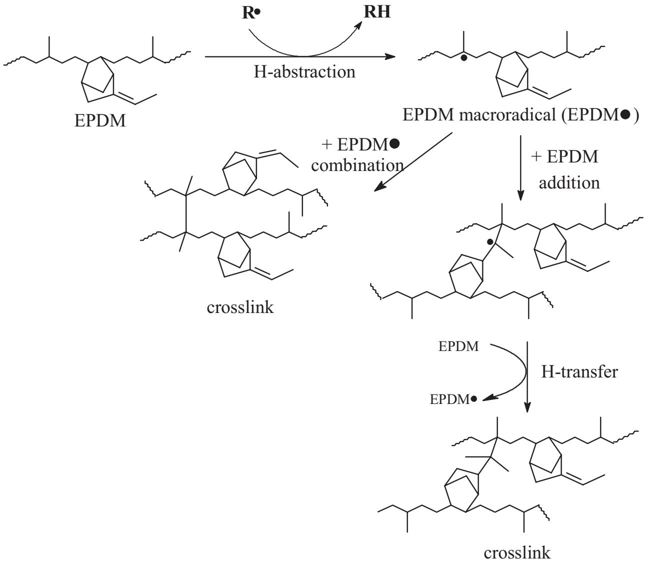

Figure 1.
Mechanism of crosslinking of EPDM in the presence of peroxide.[21]

Fourier Transformed Infrared Spectroscopy (FTIR)

Figure 2 shows attenuated total reflection infrared spectra of PMMA, AES, fraction 01 (phase extracted with hexane), fraction 02 (phase extracted with chloroform) and insoluble phase of the 6.9EPDM blend.

The spectra of the three fractions present the similar bands. The spectra present the characteristic absorption bands of polyolefin (1377 cm^{-1}), intense bands of symmetric deformation of CH_3 (1464 cm^{-1}), two characteristic absorption bands of symmetric and antisymmetric

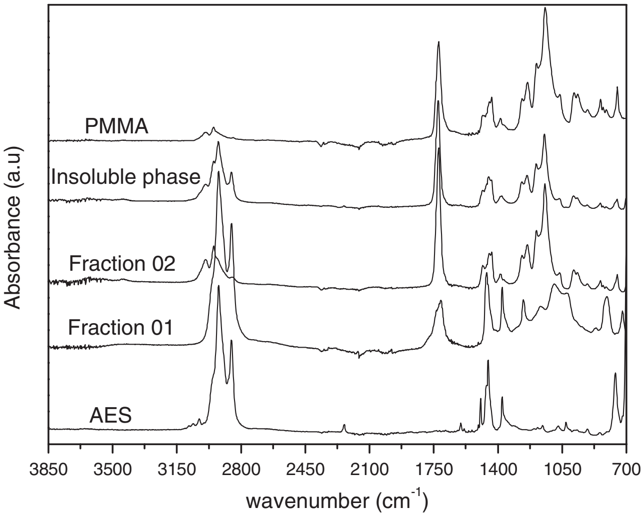

Figure 2.
ATR-FTIR spectra of PMMA, AES, fraction 01, fraction 02 and insoluble phase of 6.9EPDM blend.

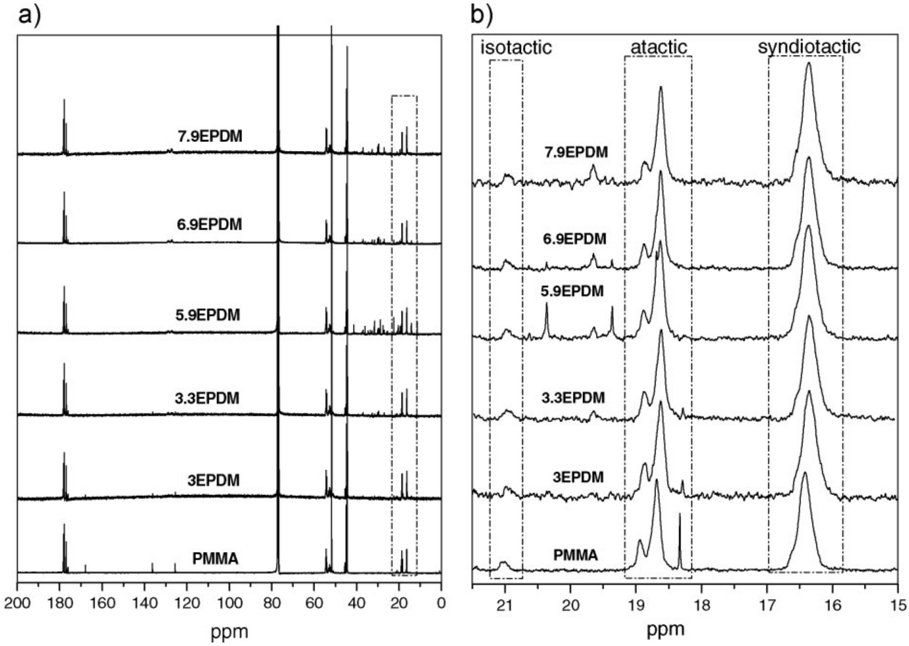

Figure 3.
^{13}C NMR spectra ($CDCl_3$) of the PMMA and PMMA-AES blends (a) Full spectrum (b) Expanded triad distribution in the α-methyl region.

stretching of EPDM (2860 and 2950 cm^{-1}),[16,22] and characteristic absorption bands of poly(methyl methacrylate) (1724 and 1390 cm^{-1}).[23] In these spectra, the absorption bands of the acrylonitrile group of SAN (2237 cm^{-1}) was not observed for the 6.9EPDM blend, because of the low SAN contents. However, this absorption can be observed in transmission infrared spectra of all fractions (data not shown).

The analysis of the spectra allows the conclusion that all fractions are mixed. However, the composition of these mixtures is variable, since the relative intensity of bands is different for each fraction. Thus, fraction 01 is richer in EPDM, while fraction 02 and insoluble fraction are richer in PMMA and maybe in SAN. These results show that PMMA-AES blends are very complex mixtures. A fraction of PMMA is grafted on EPDM and this elastomer phase is partially crosslinked (insoluble phase). Both, grafting and crosslinking of EPDM contributed to anchor the elastomer phase to the matrix.

Carbon-13 Nuclear Magnetic Resonance (^{13}C NMR)

Figure 3 shows the ^{13}C NMR spectra of the PMMA and PMMA-AES blends. The triad tacticity of PMMA was determined on the basis of the peaks of the C=O group and α-methyl group in the ^{13}C NMR spectra.[24,25] The ^{13}C NMR resonance of the ester carbonyl group is recorded in the region of 176-179 ppm and the α-methyl group is recorded in the region of 16-22 ppm.[24,26] Triad contents were estimated from integrals of C=O group and α-methyl group in the ^{13}C NMR spectra. In the ^{13}C NMR spectra is not possible to observe signals for tetrads or pentads sequences, indicatingthat the PMMA presents low stereochemistry.

The stereochemistry of the PMMA chain in the blends as determined by ^{13}C NMR using data from C=O and α-methyl regions is shown in Table 3. The total area of each analyzed region in the spectra (C=O and α-methyl regions) was assumed to be 100%.

Table 3.
^{13}C NMR triad tacticity data of the PMMA and blends.

	C=O group			α-methyl group		
	triad tacticity (%)			triad tacticity (%)		
Materials	rr	mr	mm	rr	mr	mm
PMMA	54	41	5	55	39	6
3EPDM	58	37	5	60	38	2
3.3EPDM	59	36	5	60	36	4
5.9EPDM	60	35	5	62	35	3
6.9EPDM	63	34	3	64	35	1
7.9EPDM	66	32	2	67	31	2

Table 3 shows that the amount of triad sequences calculated based on the regions of the ^{13}C NMR spectra relating to α-methyl group and C=O group are consistent with each other. The radical polymerization of the PMMA in the presence of AES produced polymers having the largest triad syndiotactic content (rr). As shown in Table 3 and Figure 4 the data for the PMMA chains indicate that an increase of the syndiotacticity was observed as the amount of AES increases.

Hirano *et al.* [27–29] proposed a mechanism for the syndiotactic-specific radical polymerization of poly(N-isopropylacrylamide) in the presence of hexamethylphosphoramide. This mechanism was adapted to explain the influence of AES on the PMMA tacticity (Figure 5).

The low stereospecificity in MMA polymerization is attributable to free rotation near the propagating chain-end (Figure 5, structure I). The rotated radical reacts with a new incoming monomer via two possible pathways. Thus, pathaway "a" should result in "*r* dyad" and pathway "b" should result in "*m* diad" (Figure 5, structure II). In the case of MMA polymerization in the presence of AES, the propagation chain-end becomes more crowded due to possible interactions between the carbonyl groups of PMMA and the nitrile or phenyl groups of SAN copolymer (Figure 5, structures III and IV). Thus, steric hindrance of the AES would limit approach via pathway "b" of the next incoming monomer. As a result, syndiotactic-specificity was induced.[27]

Dynamic Mechanical Analysis (DMA)

Figure 6 shows the dynamic mechanical behavior of PMMA and PMMA-AES blends. The storage modulus curve of PMMA shows a small drop around 0 °C, corresponding to the β-relaxation of PMMA and another drop of four orders of magnitude above 100 °C, corresponding to the glass transition of this polymer.[30]

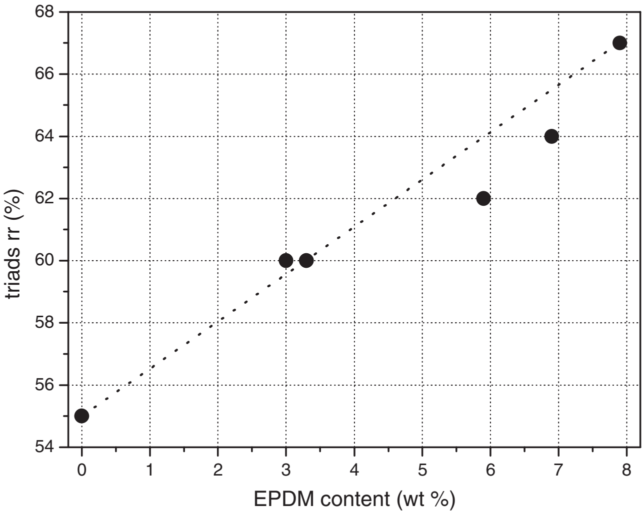

Figure 4.
Triad tacticity as a function of the EPDM content.

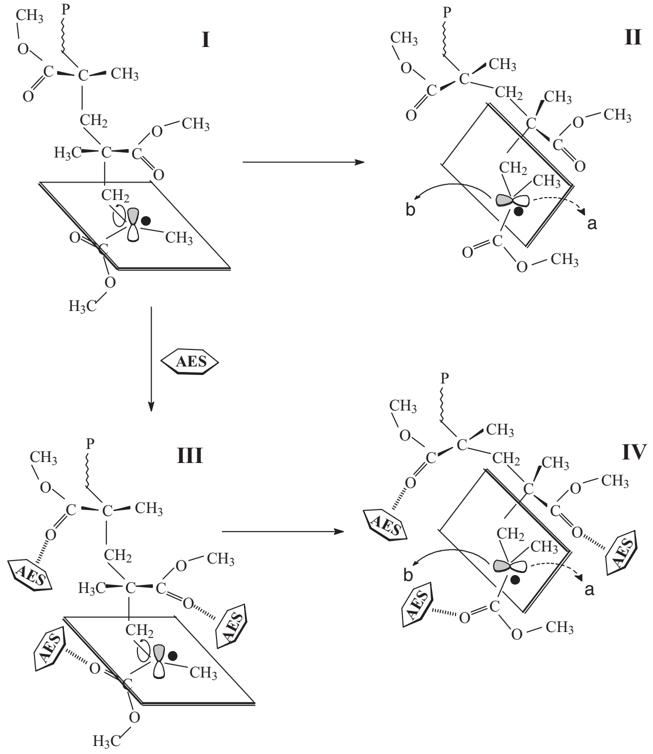

Figure 5.
Proposed mechanism for syndiotactic-specific polymerization of MMA in the presence of AES.[27]

The AES shows typical viscoelastic behavior of an unvulcanized thermoplastic elastomer: a drop of one decade around −40 °C that is due to the glass transition of the EPDM phase and another drop of two decades above 110 °C corresponding to the glass transition of the SAN phase.[13] The PMMA-AES blends show a small drop in the region of the EPDM glass transition (∼−40 °C) and a drop of three orders of magnitude at the region of the PMMA/SAN glass transition (∼120 °C). This behavior indicates that the morphology of the PMMA-AES blends is of dispersed elastomeric domains (EPDM) in a glassy matrix (PMMA/SAN).

The loss modulus curve of PMMA shows a peak around 0 °C corresponding to the β-relaxation of PMMA attributed to the rotation of the $COOCH_3$ side groups and another peak corresponding to the glass transition of PMMA at 120 °C.[30] The loss modulus of AES shows a peak at −40 °C corresponding to the EPDM glass transition and a broad peak with maximum around 60 °C that is attributed to a secondary transition of the EPDM phase. Keinath and Boyer[31] described this transition as a liquid-liquid transition, a relaxation above the glass transition temperature where the material experiences increased fluidity. The loss modulus of the PMMA-AES blends shows a peak around −40 °C corresponding to the glass transition of the EPDM phase and a peak around 120 °C corresponding to the glass transition of the PMMA/SAN phase.

The EPDM phases of all blends present a glass transition temperature at lower temperatures than the EPDM phase of AES (Figure 6(b)). This behavior was also observed in earlier work of our research group for polyhydroxybutyrate/AES blends,[32] PMMA/AES blends [15], *in situ*

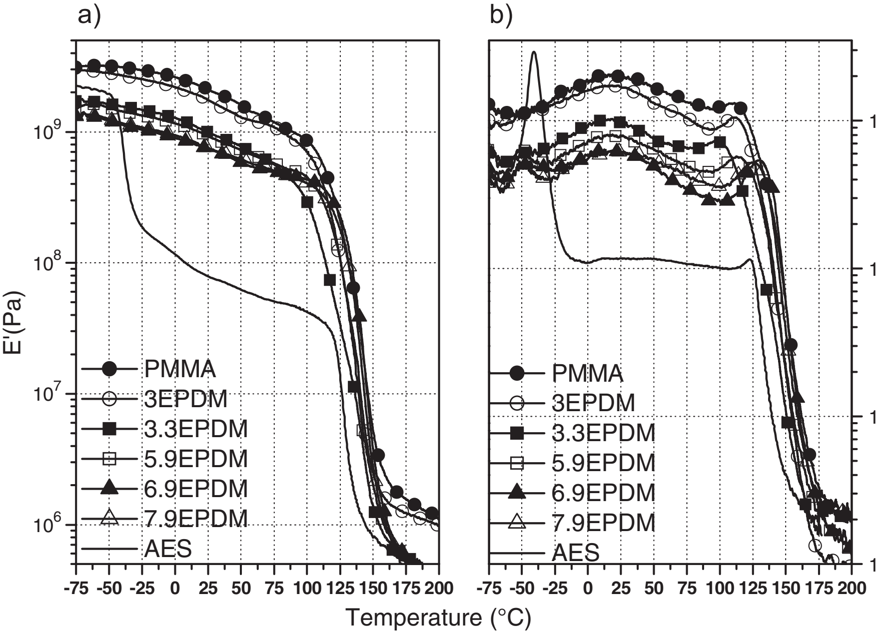

Figure 6.
Dynamic mechanical behavior of PMMA, AES and PM MA-AES blends (a) Storage modulus (E') (b) Loss modulus.

polymerized polystyrene (PS)/AES [33] and PS/EPDM.[34] This shift to lower temperatures is attributed to the phase inversion of the EPDM phase of AES due to AES dissolution in methyl methacrylate monomer and its *in situ* polymerization. EPDM is the matrix in AES (Figure 7(a)), whereas SAN and EPDM-g-SAN chains constitute the dispersed phase (Figure 7(a)). In the blends, EPDM becomes the dispersed phase (Figure 7(b)), and the release of the SAN chains from the elastomeric phase can contribute to the decreases in the EPDM glass transition temperatures.[15] This behavior in blends of a rubbery phase dispersed in glassy material is common and attributed to hydrostatic dilatational thermal stresses generated within the rubber particles because of the differences in the thermal expansion between the rubber and the glass matrix. This dilatational stress promotes an increase in the rubbery phase free volume, which allows the reduction of the relaxation time of the rubbery chains and therefore reduces the glass transition temperature of the corresponding phase.[13,35] Another condition for reducing Tg is good adhesion between the two components.[36]Thus, DMA results lead to the conclusion that some degree of miscibility between the PMMA and SAN phase of AES takes place in the blends; it may be confined to the interface, producing adhesion between the phases. The graft copolymer EPDM-*g*-SAN should promote a strong interfacial adhesion between EPDM and the matrix, since its SAN segments are dissolved in the matrix and its EPDM segments are dissolved in the elastomer phase of the blends. Besides these possibilities, infrared spectroscopy provided information about crosslinking of EPDM phase and grafting of PMMA on EPDM. Both, crosslinking and grafting should contribute to the interfacial adhesion.

The glass transitions of PMMA and of SAN are close, making it difficult to determine the extent of mixing. As can be seen in Figure 6(b), only one peak is

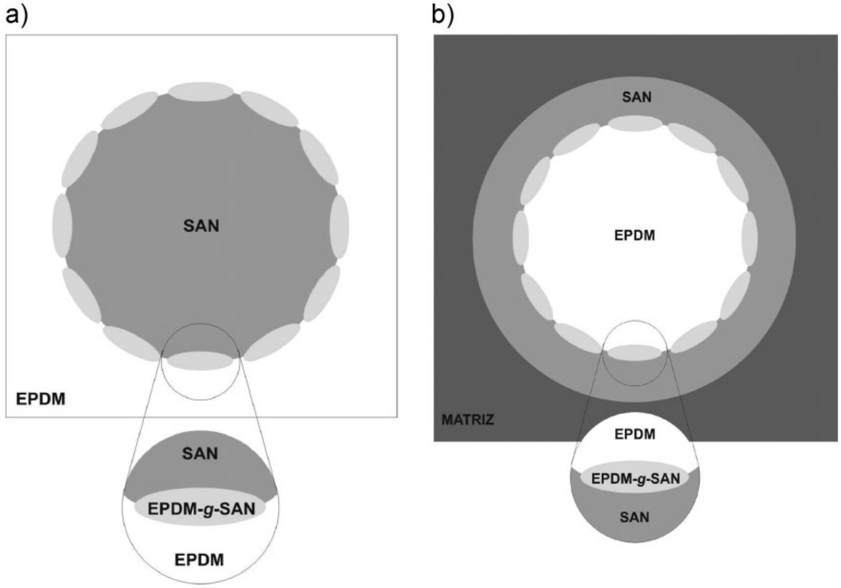

Figure 7.
Model of structure (a) neat AES (b) blend with AES.

observed in the E″xT curves in the temperature range of 75 °C and 150 °C. In same cases, for example for blend 3.3EPDM, a shoulder can also be seen. Thus, the behavior observed for PMMA-AES blends can reflect two possibilities: First, this behavior can indicate partial miscibility between PMMA and SAN, as the AN content (27%) of the SAN component used in this work is within the window of miscibility (9,5-33%). On the other hand, the peaks corresponding to the glass transition of PMMA and SAN phases can overlap.

It is possible to analyse the miscibility between the PMMA and SAN phases of AES through the additivity rule, assuming complete imiscibilitity of the blends. Figure 8 shows the comparison between simulated and experimental E″ curves of 6.9EPDM blend.

The simulated E″ curve shows a peak at 100 °C corresponding to the glass transition of the PMMA phase and a shoulder at higher temperatures corresponding to the SAN phase. However, the experimental E″ curve clearly shows a well defined peak in the temperature range of the glass transition of the PMMA and SAN, with a maximum located at intermediate temperature compared to the peaks in their simulated E″ curve. This result suggests

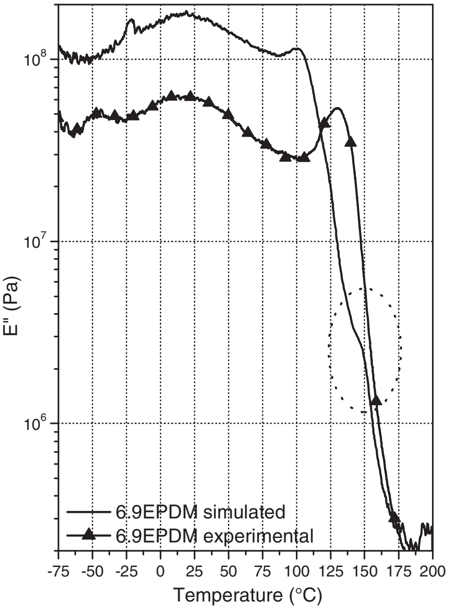

Figure 8.
Simulated E″ curve and experimental E″ curve of 6.9EPDM blend.

that there is some degree of miscibility between the PMMA and SAN phases of AES.

Transmission Electron Microscopy (TEM)

The morphologies of the PMMA-AES *in situ* polymerization blends were investigated by means of transmission electron microscopy (TEM). Figure 9 shows the TEM micrographs of PMMA-AES blends. The thin sections were stained to improve the contrast between the phases and the rubber particles (EPDM phase) became the dark phase. The morphology of PMMA-AES blends consists of an elastomeric dispersed phase in the glassy matrix, with the inclusion of matrix in the EPDM domains, suggesting a core-shell morphology, which are made up of a PMMA or SAN cores surrounded by EPDM shells. However, for the blends 6.9EPDM and 7.9EPDM it can be observed that domains became more alongated, suggesting *salami* morphology. The resulting morphologies of the *in situ* polymerized blends depend on the nature of the dissolved elastomer, initiator type, polymerization conditions and other variables.[37]

The occlusion of the glassy phase within the elastomeric domains can be due the formation of graft copolymer and/or phase inversion during polymerization.[38,39] However, the structure, with respect to grafting and crosslinking, is difficult to quantify and study, especially when conversion is high and the elastomer is crosslinked.[40] A mechanism of grafting has been reported by Arayapranee *et al.* [41] for the graft polymerization of the monomer pair styrene/MMA onto natural rubber. Adapting their approach to our system, a mechanism for the graft polymerization of MMA onto EPDM is suggested here.

During of the polymerization of PMMA-AES blends, peroxy radicals may react with the EPDM backbone, leading to a macroradical that will initiate grafting. However, the same peroxy radical may also

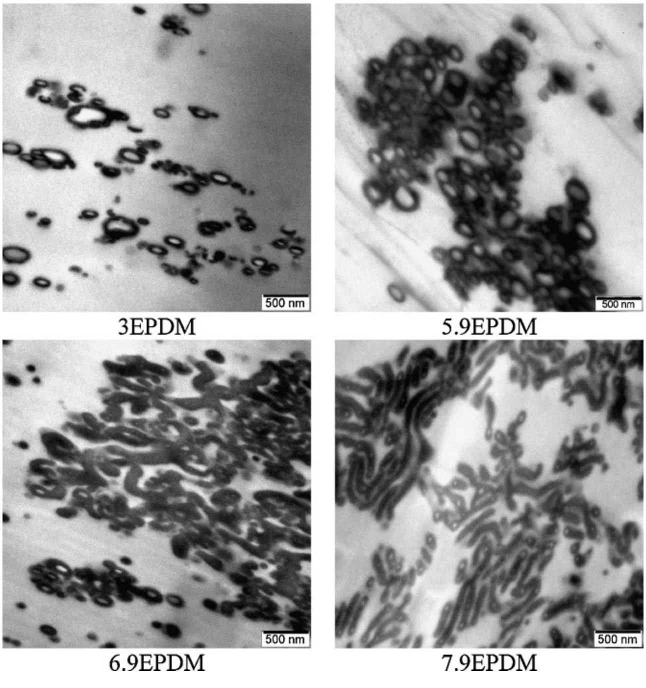

Figure 9.
TEM micrographs of PMMA-AES blends.

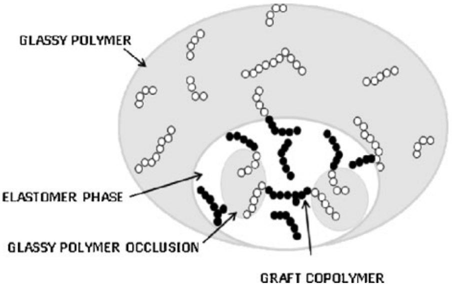

Figure 10.
Graft copolymer at the interface acting (o) segments of glassy polymer and (•) segments of elastomeric phase. (adapted from reference 42).

initiate MMA, resulting in homopolymerization. PMMA macroradicals may also combine with EPDM radicals to terminate, leading to graft copolymers. Finally, two rubber radicals may recombine leading to partial crosslinking.[42,43] Figure 10 shows the schematic representation of the interaction that occurs between the elastomeric phase and glassy phase. It is possible to observe formations of occlusion.

Besides the formation of graft copolymer, phase inversion also leads to *salami* morphology. Initially, the AES/chloroform/methyl methacrylate solutions are homogeneous, but as the concentration and molar mass of poly(methyl methacrylate) increase, phase separation occurs, leading to a system in which the continuous phase is a solution of AES/chloroform/methyl methacrylate and the dispersed phase can be a complex mixture of PMMA, SAN, EPDM, solvent and monomer. As polymerization proceeds, the amount of PMMA in the system increases and that of methyl methacrylate decreases. Therefore, the volume fraction of the PMMA-rich phase increases and that of the AES-rich phase decreases. At one point, a phase inversion occurs and the PMMA-rich phase becomes the continuous phase. The dispersed rubber particles present a complex morphology with PMMA occlusions. After phase inversion, polymerization proceeds until final conversion, trying to preserve the *salami* morphology.[38,39]

The morphologies of the polymeric blends obtained by *in situ* polymerization depend on the polymerization kinetics, polymerization degree and grafting of the reactive system, composition, miscibility, kinetic of phase separation and agitation speed.[44] The morphology of the 6.9EPDM and 7.9EPDM blends suggests that the AES/MMA/chloroform solution, initially homogeneous, undergoes spinodal decomposition due to the increase of PMMA content. This mechanism of phase separation leads to an interconnected structure. Inoue *et al*. [45] analyzed the morphological evolution of the PMMA/poly(ethylene-*co*-vinyl acetate), EVA, blend by optical microscopy and they have found that phase separation during polymerization of methyl methacrylate in the presence of EVA proceeds by spinodal decomposition.

Conclusion

The PMMA-AES blends are very complex mixture constituted by PMMA homopolymers, grafting copolymers and crosslinking. While EPDM is immiscible with other components, SAN and PMMA are partially miscible. As a result of this complexity, the morphology is also very complex reflecting the extent of crosslinking and grafting as well as phase inversion during the polymerization. The phase separation during polymerization of the MMA in the presence of AES can be interpreted in terms of a phase separation scheme based on spinodal decomposition, which is induced by the increase of PMMA content in the mixture. It has been shown that increasing the AES content of PMMA-AES blends increases the syndiotacticity of PMMA, suggesting there is some interaction between the carbonyl groups of PMMA and nitrile or phenyl groups of SAN copolymer, due to increases of syndiotacticity with increasing amounts of AES.

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[1] H. Ruckdäschel, J. K. W. Sandler, V. Altstädt, C. Rettig, H. Schmalzm, V. Abetz, A. H. E. Müller, *Polymer* **2006**, *47*, 2772.
[2] L. Corté, L. Leibler, *Polymer* **2005**, *46*, 6360.
[3] P. Poomalai, B. Ramaraj, Siddaramaiah, *J. Appl. Polym. Sci.* **2007**, *104*, 3145.
[4] S. Zheng, Q. Guo, C.-M. Chan, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2329.
[5] S. Zheng, J. Lin, Q. Guo, *J. Mater. Sci.* **1997**, *32*, 3463.
[6] E. Lourenço, M. I. Felisberti, *Eur. Polym. J.* **2006**, *42*, 2632.
[7] E. Lourenço, M. I. Felisberti, *Polym. Degrad. Stab.* **2006**, *91*, 2968.
[8] S. R. Upreti, B. S. Sundaram, A. Lohi, *Eur. Polym. J.* **2005**, *41*, 2893.
[9] L. Lalande, C. J. G. Plummer, J-A. E. MẮnson, P. Gérard, *Polymer* **2006**, *47*, 2389.
[10] R. J. Borgreeve, R. J. Gaymans, J. Sehuijer, *Polymer* **1987**, *28*, 1489.
[11] C. B. Bucknall, I. K. Partridge, M. V. Ward, *J. Mater. Sci.* **1984**, *19*, 2064.
[12] S.-K. Cheng, C.-Y. Chen, *Eur. Polym. J.* **2004**, *40*, 1239.
[13] N. M. Larocca, E. Hage, Jr, L. A. Pessan, *Polymer* **2004**, *45*, 5265.
[14] C. Saron, M. I. Felisberti, *Mater. Sci. Eng., A* **2004**, *370*, 293.
[15] R. Turchet, M. I. Felisberti, Br PI. 0305588-4, **2005**.
[16] R. Turchet, M. I. Felisberti, *Polímeros: Ciência e Tecnologia* **2006**, *16*, 158.
[17] M. Suess, J. Kressler, H. W. Kammer, *Polymer* **1987**, *28*, 957.
[18] J. Kressler, N. Higashida, T. Inoue, W. Heckmann, F. Seitz, *Macromolecules* **1993**, *26*, 2090.
[19] H. Feng, Z. Feng, C. Ye, *Polym. J.* **1996**, *28*, 661.
[20] G. N. Kumaraswamy, C. Ranganathaish, M. V. D. Urs, H. B. Ravikumar, *Eur. Polym. J.* **2006**, *42*, 2655.
[21] M. V. Duin, H. G. Dikland, *Rubber Chem. Technol.* **2003**, *76*, 132.
[22] Y. O. Bae, C. S. Ha, W. J. Cho, *Eur. Polym. J.* **1991**, *27*, 121.
[23] Y. Alias, I. Ling, K. Kumutha, *Ionics* **2005**, *11*, 414.
[24] Y. Isobe, K. Yamada, T. Nakano, Y. Okamoto, *Macromolecules* **1999**, *32*, 5979.
[25] R. C. Ferguson, D. W. Ovenall, *Macromolecules* **1987**, *20*, 1245.
[26] J-s. Wang, R. Jérôme, R. Warin, P. Teyssié, *Macromolecules* **1993**, *26*, 5984.
[27] T. Hirano, S. Masuda, S. Nasu, K. Ute, T. Sato, *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 1192.
[28] T. Hirano, H. Miki, M. Seno, T. Sato, *Polymer* **2005**, *46*, 3693.
[29] T. Hirano, S. Ishii, H. Kitajima, M. Seno, T. Sato, *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 50.
[30] F. Y. Xu, J. C. W. Chien, *Macromolecules* **1994**, *27*, 6589.
[31] S. E. Keinath, R. F. Boyer, *J. Appl. Polym. Sci.* **1981**, *26*, 2077.
[32] F. P. Carvalho, A. C. Quental, M. I. Felisberti, *J. Appl. Polym. Sci.* **2008**, *110*, 880.
[33] E. Lourenço, M. C. Gonçalves, M. I. Felisberti, *J. Appl. Polym. Sci.* **2009**, *113*, 2638.
[34] E. Lourenço, M. C. Gonçalves, M. I. Felisberti, *J. Appl. Polym. Sci.* **2009**, *112*, 2280.
[35] F. B. Bates, R. E. Cohen, A. S. Argon, *Macromolecules* **1982**, *16*, 1108.
[36] P. Szabó, E. Epacher, E. Földes, B. Pukánszky, *Mater. Sci. Eng., A* **2004**, *383*, 307.
[37] H. F. Mark, N. M. Bilakes, C. G. Overberger, *Encyclopedia of Polymer Science and Engineering*, John Wiley & Sons, Inc., New York 1998.
[38] G. P. Leal, J. M. Asua, *Polymer* **2009**, *50*, 68.
[39] S. J. Lee, H. G. Jeoung, K. H. Ahn, *J. Appl. Polym. Sci.* **2003**, *89*, 3672.
[40] K. S. Jagadeesh, Siddaramaiah, V. Kalpagam, *J. Appl. Polym. Sci.* **1990**, *40*, 1281.
[41] W. Arayapranee, P. Prasassarakich, G. L. Rempel, *J. Appl. Polym. Sci.* **2002**, *83*, 2993.
[42] V. G. Grassi, M. M. C. Forte, M. F. D. Pizzol, *Polímeros: Ciência e Tecnologia* **2001**, *11*, 158.
[43] D. L. Tillier, J. J. Meuldijk, G. W. H. Höhne, P. M. Frederik, O. Regev, C. E. Koning, *Polymer* **2005**, *46*, 7094.
[44] D. Klempner, L. H. Sperling, L. A. Utracki, *Interpenetrating Polymer Networks*, 1° Ed., Ed. ASC, Washington, 1994.
[45] T. Inoue, S. Kobayashi, W. Chen, T. Ohnaga, T. Ougizawa, *Polymer* **1994**, *35*, 4015.