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# On the Production of Compatibilized Polyethylene Terephthalate – Styrene Butadiene Rubber Blends

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**ABSTRACT:** Styrene-butadiene rubber (SBR) is chemically modified with maleic anhydride (MAH) in a continuous process (reactive extrusion) at three different extrusion speeds with and without reaction initiator (benzoyl peroxide). The resulting modified rubber is used to produce compatibilized blends with polyethylene terephthalate (PET). The amount of grafted MAH groups on the rubber is determined by chemical titration and the degree of grafting is measured by infrared analysis. The degree of compatibilization between SBR and PET is determined indirectly through measurements of mechanical properties and average molecular weight of the blends. The anhydride and peroxide concentration influences the grafting reaction strongly and hence the mechanical properties and impact resistance of the blends. Compatibilization of the elastomeric and plastic phases at specific processing conditions gives rise to large improvements in the impact resistance of the blend over that of PET alone. © 2000 John Wiley & Sons, Inc. *Adv Polym Technol* 19: 34–40, 2000

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## Introduction

The blending of polymers is a topic broadly investigated because of the low cost, excellent properties, and benefits that may be obtained in

blends possessing chemical or physical compatibility. Unfortunately, most polymers are thermodynamically incompatible. When they are mixed, the free energy  $\Delta G_m$  of the system is positive, which leads to phase separation manifested as a reduction of the blend properties as compared to those of the polymers alone. In the particular case of the blends analyzed in this work, styrene butadiene rubber (SBR) is incompatible with polyethylene terephthal-

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ate (PET), and consequently the blend of these polymers possesses low mechanical properties. The improvement of mechanical and impact properties requires higher miscibility among the different phases. The method followed here involves the grafting of the rubber with maleic anhydride (MAH) to build chemical links between rubber and polyester. The grafting process is carried out by a free radical reaction between the anhydride and the rubber, with the addition of benzoyl peroxide (BPO) as initiator.<sup>1</sup> BPO and other peroxides have been used extensively as reaction initiators and/or crosslinking agents and several works have dealt with the use of peroxides in grafting reactions.<sup>1,2,3</sup> Comparisons on the efficiency of two peroxides<sup>1</sup> (AIBN and BPO) reveal that in the grafting reaction of MAH with SBR, BPO renders better results. Furthermore, BPO is more efficient than dicumyl peroxide (DCP) in the reaction of MAH with EPDM.<sup>3</sup> In several works, an extruder is used to provide the thermomechanical stresses necessary to induce the reaction.<sup>4,5</sup> To systematically evaluate the extent of the reaction in this work, the reactive extrusion is performed using three extrusion speeds (30, 70, and 100 rpm) to obtain an entire grafting profile of the anhydride on the rubber. The concentration of maleic anhydride and peroxide affects the average molecular weight and the grafting of MAH on the vinyl groups of the rubber. Thereafter, the reaction of the modified rubber with PET is carried out in a twin screw extruder to obtain the resulting blend.

## Experimental Procedure

### MATERIALS

PET from Celanese (Mexico) possesses a density of 1.425 g/cm<sup>3</sup> according to the ASTM D792 norm, melting point of 240°C (determined by DSC), crystallinity of 37% (also determined by DSC<sup>6,7</sup>) intrinsic viscosity<sup>8</sup> of 0.850 dl/g, and average molecular weight ( $\bar{M}_w$ ) of 26000 g/mol as measured by high temperature GPC using m-cresol. SBR from Negromex (Solprene 416) has a density of 0.919 g/cm<sup>3</sup> (ASTM D792), styrenic block<sup>9</sup> of 30% weight,  $\bar{M}_w$  of 105,400 (as determined by high temperature GPC using 1,2,4 trichlorobenzene) and a glass transition temperature of -89°C (measured by DSC). The additives used to prevent oxidation are Irganox 1076 for the rubber and Irganox 1010 for PET, from Ciba-Geigy. BPO was obtained from Promoters and Or-

ganic Catalysts, and the maleic anhydride (MAH) was obtained from Baker.

### EQUIPMENT

A Haake Rheocord 90 twin-screw conical counter-rotating extruder with 331 mm length, model TW100, was used in the reactive extrusion process. A dehumidifier (Pagani DHF) with molecular meshes was employed to dry the materials. Specimens for impact and tensile tests were made in an injection-molding machine Demag Ergotech 50. An Instron machine model 1125 was employed for tensile tests following ASTM D638. Impact tests (Izod notched) were carried out following ASTM D256-92. Molecular weights were measured in a high temperature GPC Waters model 150-C ALC/GPC. The infrared spectrometric analysis was performed in a FTIR Nicolet model 510-P.

### GRAFTING REACTION

SBR was dried at 80°C for 6 hours. Mixtures of BPO and MAH with SBR were fed to the extruder at 160°C. Extruder rotational speeds used were 30, 70, and 100 rpm. The amount of MAH used in the grafting reaction ranged from 0 to 3.5 phr (g MAH/100g SBR). BPO concentrations considered were 0, 3, 7, and 10% with respect to the MAH weight.

The extent of the MAH-SBR reaction is determined by measuring the acid number.<sup>10</sup> This is obtained by dissolving a gram of grafted rubber in 100 ml of toluene with reflux at 65°C for three hours. Subsequently, 50 ml of water are added and three different phases form: organic, gel, and aqueous. The organic phase contains the rubber grafted with MAH, the gel phase contains the crosslinked rubber, and the aqueous phase contains the MAH which did not react and remains dissolved in water. From the organic phase, an aliquot is titrated with a KOH solution in ethanol using 0.1 N thymol blue indicator. An excess of 0.5 ml of KOH is added to the solution (we observe a change of color to blue) and then it is re-titrated with HCl up to 0.05 N (until the color changes to yellow). The acid number and the percentage of MAH that reacted are calculated according to the following relations:

$$\begin{aligned} \text{Acid number (mg KOH/g rubber)} \\ = \text{ml KOH} * \text{N KOH} * 56.1 / 1 \text{ g SBR} \quad (1) \end{aligned}$$

$$\begin{aligned} \% \text{ MAH that reacts} = (\text{Acid number}) * (98) \\ / ((2) * (56.1)) * (\text{g SBR} / \text{g MAH}) \quad (2) \end{aligned}$$

Taking into consideration that the styrene weight percentage in SBR is 30%, calculation of the number of butadiene and MAH moles taking part in the reaction is given by:

$$\eta \text{ BUTADIENE} = (\text{Weight of SBR} - \text{Weight of styrene}) / 57760 \text{ g/mol} \quad (3)$$

$$\eta \text{ MAH} = \text{Weight of anhydride added} / 98 \text{ g/mol} \quad (4)$$

The number of MAH moles that have reacted is defined as:

$$\text{MAH reacted} = \eta \text{ MAH added} * \% \text{ of MAH reacted} \quad (5)$$

and the graft efficiency can be expressed as:

$$\% \text{ graft MAH} = (\eta \text{ MAH reacted} / \eta \text{ butadiene rubber}) * 100 / 1069 \quad (6)$$

Finally, the number of grafted moles of MAH per mole of BPO are calculated as follows:

$$\eta \text{ BPO added} = (\text{weight of MAH added} * \% \text{ BPO}) / 242 \text{ g/mol} \quad (7)$$

$$\text{MAH/BPO} = \eta \text{ MAH reacted} / \eta \text{ BPO added} \quad (8)$$

It is necessary to point out that measurements of the MAH grafting-reaction efficiency through titration are well known.<sup>1,2,10</sup> Some methods which require careful manipulations were followed in this work.

### BLENDING PROCEDURE

PET is dried for 12 hours at 120°C. The mixture of PET with 10 phr of SBRg is processed in a twin screw extruder with a speed of 50 rpm at 270°C. The grafting reaction on the rubber and the extrusion speed allowed an adequate dispersion of the rubber particles in the PET matrix. These have an average particle size of 6.7 E-06 m.

## Results and Discussion

As is well known, the anionic polymerization of butadiene can be carried out via 1,4 or 1,2 addition

routes (see Figure 1). Through 1,4 addition, linear polybutadiene is obtained (cis or trans) and through 1,2 addition, branched polybutadiene with mostly vinyl groups is obtained.<sup>11</sup> Because SBR presents a mixture of linear and branched molecules, the grafting of MAH can take place on either linear chains or chains with vinyl groups.

Results of the percentage of MAH-grafted groups on SBR are shown in Table I. Column A indicates the screw speed and amount of benzoyl peroxide used in the reactive extrusion, column B indicates the amount (mg) of KOH used for titration of one gram of SBRg, column C indicates the amount of MAH that reacts in the organic phase as a percentage of total MAH added, column D represents the percentage of MAH which has reacted with SBR, and column E shows the amount of reacted MAH per mole of added peroxide. The largest amount of reacted MAH per mole of BPO is obtained with 3% of the BPO/MAH ratio for the three extrusion speeds. This indicates that peroxide concentration affects the efficiency of the grafting reaction. Table I also shows that the reaction can be accomplished without BPO, since free radicals can also be produced by the energy provided by the thermomechanical work in the extruder. In column D, the grafted butadiene percentage (main chain and branched vinyl groups) is shown, assuming that a single molecule of MAH reacts with a double bond. As observed, when the peroxide amount is increased, the number of grafted molecules varies for the three extrusion speeds. The grafting degree of MAH lies approximately between 0.6 and 0.8, implying similar reaction kinetics. The average resi-

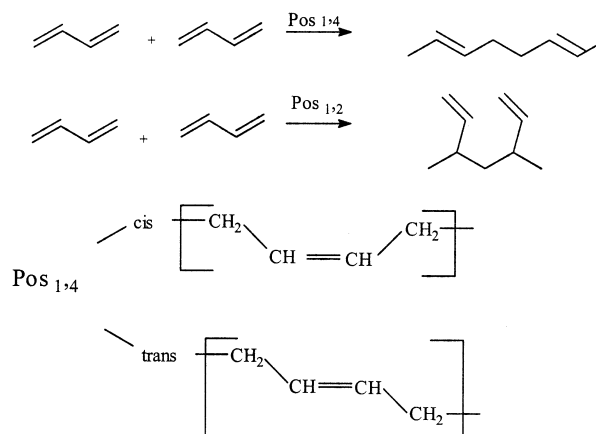


FIGURE 1. Schematic representation of SBR polymerization.

**TABLE I**  
**Results of the Reaction of MAH with SBR. MAH Concentration is 2g MAH/100g SBR (2 phr).**

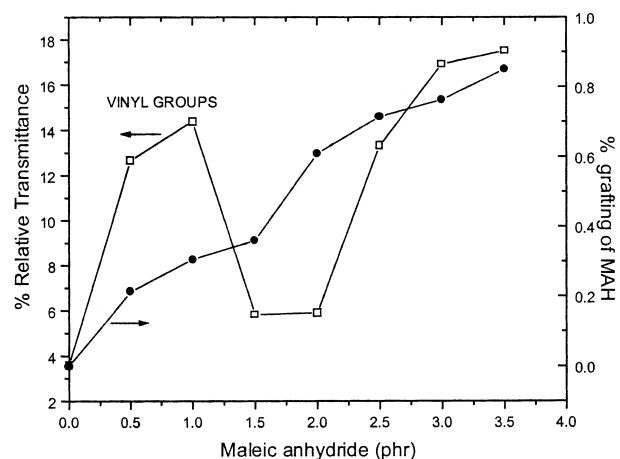
Processing Conditions		Acid Number	% of Reacted MAH	% Grafting	Mole of MAH Reacted/ Mole of BPO
A		B	C	D	E
RPM	%BPO/MAH	mg KOH/g rubber	%	%	
30	0	9.82	42.90	0.675	—
30	3	9.61	41.98	0.661	34.55
30	7	10.80	47.16	0.742	16.64
30	10	8.63	37.69	0.593	9.308
70	0	8.70	37.99	0.598	—
70	3	8.84	38.61	0.608	31.78
70	7	10.80	47.16	0.742	16.64
70	10	10.10	44.12	0.695	10.89
100	0	9.96	43.51	0.685	—
100	3	11.86	51.78	0.815	42.62
100	7	9.54	41.65	0.656	14.70
100	10	10.60	46.27	0.728	11.42

dence time in the extruder for SBR, MAH, and BPO mixture is 1, 2, and 3 minutes, respectively, for the three extrusion speeds of 30, 70, and 100 RPM. Although the half-life time of the benzoyl peroxide<sup>12</sup> is about six seconds at 160°C, this period is sufficient to induce the grafting reaction of the anhydride. Otherwise, the degree of grafting of MAH on SBR would not increase, as the MAH content is increased in the reaction.

### INFRARED ANALYSIS AND AVERAGE MOLECULAR WEIGHT

FTIR has been used with excellent results in mixtures of maleic anhydride, peroxides, and elastomers.<sup>1,3</sup> Results of the SBR infrared spectra show a strong peak at 968  $\text{cm}^{-1}$  due to the presence of vinyl groups. A decrease in the magnitude of this peak may be related to the consumption of these groups due to their reaction with MAH. In Figure 2, an increase in the relative transmittance is observed. The relative transmittance is a comparison of transmittance intensities of one peak at 2930  $\text{cm}^{-1}$  (which corresponds to the non-reacted C-H groups) and another peak at 968  $\text{cm}^{-1}$  (corresponding to vinyl groups). The maximum in the curve at 1% MAH concentration signals the highest consumption of vinyl groups due to the grafting reac-

tion with MAH. These data further indicate that the initial preferential site for the grafting reaction occurs on the vinyl groups. Notice that from 1.5 to 2% MAH concentration the consumption of vinyl groups go through a minimum, which indicates that the grafting reaction now takes place on the main chain double bonds and not on the vinyl branches.



**FIGURE 2.** Effect of the MAH–SBR reaction on the vinyl groups concentration from the infrared spectra at 968  $\text{cm}^{-1}$ . Percent relative transmittance (consumption of vinyl groups) as a function of MAH content.

For higher MAH concentrations, the depletion of the vinyl groups increases once more, which implies that the reaction is no longer occurring on the main chain unsaturations, since the percentage of grafting on SBR as a function of MAH concentration is a steady increasing function over the whole range of MAH concentrations.

In Table II the variation of  $\bar{M}_w$  of SBR-g and also of the resulting PET–SBRg blend with 10 phr SBRg content are shown as a function of MAH concentration. These results are obtained with a 3% BPO/MAH ratio and an extrusion speed of 70 rpm. As observed, the amount of MAH affects the molecular weight of the rubber and that of the blend considerably. When the concentration of 2 phr of MAH is exceeded, the molecular weight of the PET–SBRg blend decreases strongly. It is noteworthy that the pronounced decrease in molecular weight takes place over the concentration range past the minimum in Figure 2, which indicates that the reaction on the vinyl groups affects strongly the molecular weight of the resulting blend. This implies that as the concentration of reacted vinyl groups with MAH increases, interactions with PET are modified and hence the properties of the material are changed. Apparently an excess of grafted vinyl groups affects the average molecular weights of both SBR and the SBR–PET blend, reducing the magnitude of the mechanical and impact properties. On the other hand, as observed in Table II, the largest molecular weight of the PET–SBRg blend shows up at 2 phr of MAH, when the impact properties achieve the optimum value.

As mentioned, the percentage of grafting of MAH groups on SBR increases in accordance with

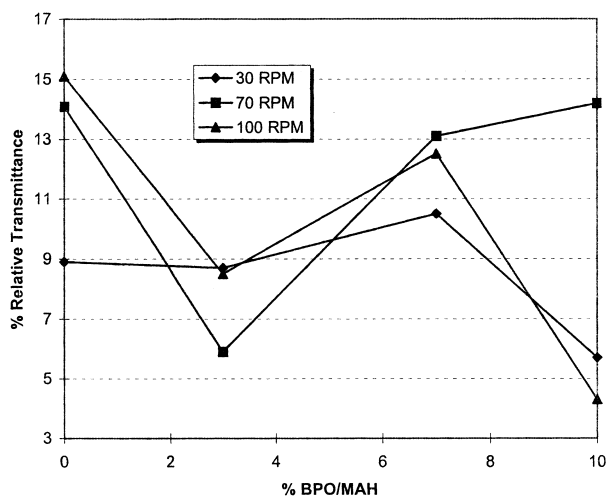
a larger amount of MAH in the mixture. The biggest grafting percentage does not provide the best impact properties of the blend.

The decrease of mechanical properties of blends due to an excessive amount of functional groups has been reported in experiments in which other mechanical properties, such as adhesion strength, were determined. For example, in PVC–maleic acid/aluminum systems, PMMA–acrylamide/steel–epoxy, as well as in adhesive joints of irradiated PP.<sup>13</sup>

Figure 3 shows results of infrared analysis by plotting the percentage of relative transmittance of vinyl groups as a function of BPO concentration, for various extrusion speeds, using 2 phr of MAH. As observed, given a fixed amount of MAH, BPO concentration is the main factor that influences the grafting reaction on the vinyl groups. The grafting reaction may be activated without peroxide, and in this case the reaction of MAH on vinyl groups is preferred. The concentration of grafted groups produces important effects on the inherent properties of the material (bulk properties). Apparently, from the results obtained at some BPO concentrations, the peroxide behaves more as an inhibitor than a promoter of the grafting reaction and there is a specific BPO concentration at which a maximum grafting is obtained. Notice that at 70 rpm with a 3% BPO concentration the relative transmittance goes through a minimum, which implies the presence of a large concentration of non-reacted vinyl groups (low consumption of vinyl groups) and therefore the reaction takes place on the main chain. At these conditions, the small amount of grafted vinyl groups in SBR and the dominating grafting on the main chain

**TABLE II**  
**Properties of the SBRg–PET Blend. Conditions of the Grafting Reaction: rpm = 70, BPO/MAH = 3%, T = 160°C.**  
**Conditions of Blending: rpm = 50, SBRg/PET = 10 phr, T = 270°C.**

MAH phr	Young's Modulus MPa	Tension Strength MPa	Izod Impact Notched J/m	$\bar{M}_w$ SBRg g/mol	$\bar{M}_w$ PET–SBRg g/mol
0	*	*	38	105400	*
0.5	911	42	77	133900	77600
1.0	931	42	69	107100	65000
1.5	933	42	64	127900	64400
2.0	700	39	104	109300	192300
2.5	520	35	68	186100	46600
3.0	420	28	75	180100	36100
3.5	200	25	45	155100	80900



**FIGURE 3.** Effect of BPO concentration on the amount of vinyl groups (percent relative transmittance) in SBRg for various extrusion speeds.

induces the highest degree of compatibility with PET. In this case, the blend molecular weight is also the highest (~ 190 000).

Table III presents molecular weight results of grafted SBR and PET–SBRg blends as a function of BPO amount, keeping the MAH concentration fixed (2 phr). As expected, the molecular weight of SBR does not present large changes, because the percentage of MAH graft is small (less than 1%). On the other hand, the maleated SBR–PET blend in the presence of BPO (3%) and processed with an extrusion speed of 70 rpm renders a blend with high molecular weight. This property influences positively the mechanical behavior and the impact resistance

of the blend with PET (104 J/m with a rubber content of 10 phr and 123 J/m for 15 phr), which presents an outstanding increase in the impact resistance as compared with that of PET alone (52 J/m).

## Conclusions

The grafting reaction of MAH on SBR affects the average molecular weight of SBR and that of the PET–SBRg blends. The SBRg with the highest molecular weight does not necessarily produce the best results in blends with PET. However, the blend with the largest molecular weight obtains the best impact resistance results. Molecular weights obtained as a function of BPO concentration indicate that with a 3% BPO/MAH ratio and with 2 phr MAH content, the optimum processing conditions for the grafting reaction with SBR are obtained at 70 rpm. The vinyl groups concentration of SBR is affected directly by the MAH and BPO contents. The compatibility achieved in the PET–SBRg blends increases the impact resistance from 52 J/m to 123 J/m. The largest increase in molecular weight of the PET–SBRg blend was not obtained with the SBR possessing the largest amount of grafted groups. When BPO is not used in the grafting reaction, MAH is grafted on the vinyl groups preferentially.

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**TABLE III**  
Average Molecular Weight of the PET–SBRg Blends and SBRg Obtained at Different Extrusion Speeds as a Function of the BPO Concentration for a Fixed MAH Content (2 phr).

% BPO/ MAH	PET–SBRg	PET–SBRg	PET–SBRg	SBRg	SBRg	SBRg
	Blend 30 RPM	Blend 70 RPM	Blend 100 RPM	30 RPM	70 RPM	100 RPM
	$\bar{M}_w$ g/mol	$\bar{M}_w$ g/mol	$\bar{M}_w$ g/mol	$\bar{M}_w$ g/mol	$\bar{M}_w$ g/mol	$\bar{M}_w$ g/mol
0	123500	80200	112000	114200	114400	106700
3	101000	192300	85000	103000	109300	117000
7	96400	159000	110800	111900	106600	148200
10	131500	99700	129800	93700	134700	142800

also in the IR and GPC sample preparation. We also thank Mr. Miguel Canseco for the infrared spectra analysis and Juan García for the molecular weight determinations by GPC.

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