

# Styrene-Assisted Grafting of Maleic Anhydride onto Polypropylene by Reactive Processing

S. H. P. Bettini,<sup>1</sup> A. C. Ruvolo Filho<sup>2</sup>

<sup>1</sup>Centro Universitário da FEI, Avenida Humberto de Alencar Castelo Branco 3972, São Bernardo do Campo, São Paulo, Brazil, CEP 09850-901

<sup>2</sup>Departamento de Química, Universidade Federal de São Carlos, Rodovia Washington Luiz km 235, São Carlos, São Paulo, Brazil, CEP 13565-905

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**ABSTRACT:** The grafting of maleic anhydride (MA) onto polypropylene (PP) was performed in the presence of the electron-donating monomer styrene (ST) according to a central composite experimental design, in which the initial MA and ST concentrations were varied. The grafting of MA onto PP in the absence of ST was also performed. All reactions were carried out in the molten state in a Haake rheometer. The amount of reacted MA and the extent of degradation in PP were determined by means of Fourier transform infrared spectroscopy and melt flow index (MFI) measure-

ments, respectively. The results showed that the presence of ST in the reactive processing caused a reduction in MFI and an increase in the level of reacted MA when the initial MA concentration equaled the initial ST concentration. An increase in the initial MA concentration presented distinct behavior that depended on the ST content. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1430–1438, 2008

**Key words:** functionalization of polymers; graft copolymers; poly(propylene) (PP); reactive processing

## INTRODUCTION

The grafting of maleic anhydride (MA) onto polypropylene (PP) in the melt has been the subject of several investigations in recent decades.<sup>1–7</sup> The interest in this field may be due to the increasing use of the obtained grafted copolymer as a compatibilizer between polar and nonpolar polymers<sup>8,9</sup> and as a coupling agent between nonpolar polymers and inorganic fillers.<sup>10,11</sup>

The grafting optimization of MA onto PP involves many variables. The conversion rates of this reaction are, however, very low. Among the many variables affecting this reaction, peroxide concentration ( $C_{PER}$ ) is that which has resulted in the highest percentage of reacted maleic anhydride ( $\%MA_r$ ); however, an increase in this variable leads to pronounced PP degradation.<sup>5–7</sup>

Several studies have been done to maximize  $\%MA_r$  and minimize PP degradation by  $\beta$  scission. Machado et al.<sup>12</sup> and Cha et al.<sup>13</sup> investigated the effect of processing conditions on  $\%MA_r$ . In both investigations,  $\%MA_r$  in PP was shown to be affected by screw con-

figuration and increased along the extruder up to length/diameter values ranging from 15 to 20, above which it remained practically constant. In other investigations, researchers proposed the incorporation of a comonomer with the MA to increase reactivity toward PP.<sup>14–18,21</sup>

According to Hu et al.,<sup>14,15</sup> one way to minimize degradation would be through the activation of the MA double bond, which would make it more reactive toward PP, increase the grafting efficiency, and reduce chain scission. One of the possible routes for activating MA would be the addition of an electron-donating monomer, such as styrene (ST), which is able to form a charge-transfer complex (CTC) with MA. In their investigations, the presence of ST in the PP–MA–peroxide system increased the grafting efficiency and reduced PP degradation.

Other systems have been tested. Sun et al.<sup>16</sup> and Cartier and Hu<sup>17</sup> investigated the reaction of glycidyl methacrylate on PP in the presence of ST and also observed an increase in the grafting reaction and a reduction in PP degradation when compared to the reaction performed without ST. The grafting of MA and  $\alpha$ -methylstyrene onto atactic PP was investigated by Braun et al.<sup>18</sup>

In this study, the grafting of MA onto PP in the presence of ST was conducted in the molten state, where the effects of initial maleic anhydride concentration ( $C_{MA}$ ) and initial styrene concentration ( $C_{ST}$ ) on  $\%MA_r$  and the melt flow index (MFI) were analyzed. The investigation was conducted according to

Correspondence to: S. H. P. Bettini (silvia.bettini@uol.com.br).

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an experimental design to study the effect of the independent variables and their interactions on the responses (%MA<sub>r</sub> and MFI) over a wide experimental range. One of the aims in our study was to examine the influence of the comonomer concentrations in the reaction, whereas Hu et al.<sup>14,15</sup> maintained equimolar ratios of MA to ST.

## EXPERIMENTAL

### Materials

PP was supplied by Suzano Petroquímica (Mauá, Brazil), under code JE-6100, with a MFI of 2 g/10 min. The MA used was from Riedel-de Haen (Seelze, Germany) and had 99% purity; ST monomer was supplied by Central Polímeros da Bahia (Camaçari, Brazil). The peroxide selected for our investigation was a 46.5% concentrate of 2,5-dimethyl-2,5-di(*t*-butyl-peroxy) hexane in CaCO<sub>3</sub>, which was supplied by Elf Atochem Brasil Química, Ltd. (Luperox 101 XL) (Rio Claro, Brazil).

The ST used was distilled in the laboratory to remove polymerization inhibitors commonly added for storage purposes.

### Methods

#### Reactive processing

MA grafting reactions onto PP in the presence of ST were conducted in a Haake torque rheometer (Karlsruhe, Germany) equipped with a Rheomix 600p mixing chamber under the following process conditions: reaction temperature, 180°C; rotor frequency, 55 rpm; reaction time, 10 min; and N<sub>2(g)</sub> atmosphere. Experiments were performed according to a central composite design, with initial C<sub>MA</sub> and C<sub>ST</sub> values as variables (Table I). All formulations were processed in duplicate to enable the calculation of the standard deviation from reactive processing. The central composite design was an experimental statistical design consisting of a two-level factorial design (experiments 1–4 in Table I), central points (experiments 5 and 6), and a star design (experiments 7–10). The central composite design and the results obtained allowed us

**TABLE I**  
Central Composite Design

Run	C <sub>PER</sub> (phr)	C <sub>MA</sub> (phr)	C <sub>ST</sub> (phr)
1	0.1	1.5	1.5
2	0.1	6.5	1.5
3	0.1	1.5	6.5
4	0.1	6.5	6.5
5	0.1	4.0	4.0
6	0.1	4.0	4.0
7	0.1	0.5	4.0
8	0.1	7.5	4.0
9	0.1	4.0	0.5
10	0.1	4.0	7.5

**TABLE II**  
Reference Formulations

Run	C <sub>PER</sub> (phr)	C <sub>MA</sub> (phr)	C <sub>ST</sub> (phr)
11	0	0	0
12	0.1	0	0
13	0.1	0.5	0
14	0.1	1.5	0
15	0.1	4.0	0
16	0.1	6.5	0
17	0.1	7.5	0
18	0.1	0	0.5
19	0.1	0	1.5
20	0.1	0	4.0
21	0.1	0	6.5
22	0.1	0	7.5

to model the behavior of the investigated responses and allowed us to construct and analyze the response surface graphs.<sup>19</sup>

PP was placed in the mixing zone and left to melt for 1.5 min. Subsequently, a PP bag containing monomers (MA and ST) previously cooled in liquid nitrogen and peroxide was added. Cooling was performed to the lower monomer temperature up to incorporation into the reaction mass and to minimize monomer evaporation.

In addition to the central composite experimental design, all reference formulations were processed in the torque rheometer. The reference formulations are listed in Table II and included PP and MA formulations without ST and in the presence of peroxide, and PP and ST formulations without MA and in the presence of peroxide.

After processing, the samples were pressed into thin sheets at 180°C to facilitate cutting into small pellets.

#### Purification method

To assess %MA<sub>r</sub> by Fourier transform infrared (FTIR) spectroscopy, the purification of the modified PP was carried out by the removal of unreacted MA, ST, MA oligomers and styrene–maleic anhydride copolymers (SMAs) in the polymer mass. Only ungrafted and grafted PP were precipitated in acetone, that is, PP, PP-g-MA, PP-g-ST, and PP-g-maleic anhydride-styrene copolymer (MAST), whereas the oligomers, homopolymers, and copolymers of MA and ST were soluble in acetone. Hence, after purification, %MA<sub>r</sub> could be assessed.

The purification method we used consisted of solubilization in xylene and precipitation in acetone (twice); 4 g of PP-g-MAST or PP-g-MA (reference formulations) was dissolved in 400 mL of xylene under reflux at 130°C for 1 h. The temperature was lowered, and acetone was added. The precipitate was vacuum-filtered and washed several times with acetone. The sample was then left in a vacuum oven for solvent removal.

After that, the purified samples were pressed into films in a Luxor press (São Paulo, Brazil) at 190°C and 100 Kg/cm<sup>2</sup> and were then submitted to heat treatment at 125°C for 24 h to convert succinic acid groups into anhydride groups.

#### FTIR spectroscopy

Transmittance analyses were performed in a Nicolet Magna IR 750 spectrophotometer (Madison, WI) with a resolution of 2 cm<sup>-1</sup> and 128 scans per spectrum. Analyses were done in triplicate.

When the analysis of grafted MA onto PP was performed in the PPs functionalized with MA only, the carbonyl absorbance was measured at 1789.6 cm<sup>-1</sup>, and when ST was present, carbonyl absorbance was measured at 1780.9 cm<sup>-1</sup>.

Analyses of these bands allowed us to calculate the carbonyl index (CI):

$$CI_{MA} = \frac{A_{1789.6}}{A_{1167}} \quad (1)$$

$$CI_{MA-ST} = \frac{A_{1780.9}}{A_{1167}} \quad (2)$$

where  $A_{1167}$  is the characteristic absorbance of CH<sub>3</sub> groups proportional to the amount of PP.

%MA<sub>r</sub> values, in the absence and in the presence of ST, were obtained by calibration curves plotted from blends of PP–dodecenyl succinic anhydride (DSA) and PP–MAST, respectively.

The relative amount of ST present in the sample could also be obtained by infrared spectra as follows:

$$\text{Relative amount of ST} = \frac{A_{704}}{A_{1167}} \quad (3)$$

where the 704-cm<sup>-1</sup> band attributed to the ST C—C bonds in MAST.

#### MFI

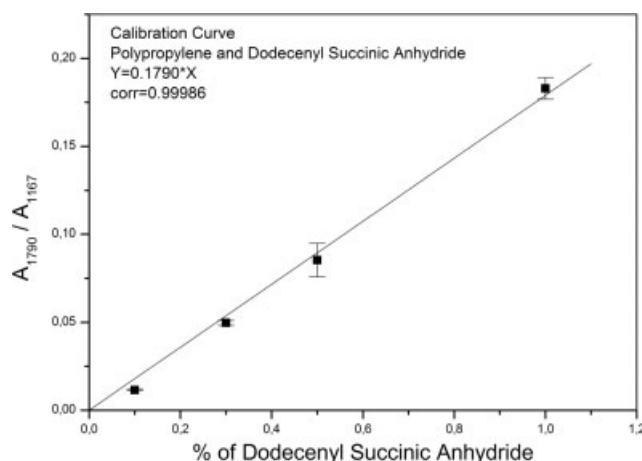
The measurement of MFI (230°C and 2.16 Kg) was performed in a Davenport plastometer (Harts, England) according to ASTM D 1238 to verify the extent of PP degradation. Analyses were performed in triplicate.

#### Construction of calibration curves

Calibration curve of the MA amounts in PP in the absence of ST

To construct the FTIR calibration curves, blends of known PP and DSA amounts were processed in the Haake rheometer.

The DSA contents in PP were as follows: 0.1, 0.3, 0.5, and 1 wt %.



**Figure 1** Calibration curve of %MA<sub>r</sub> (succinic anhydride) in PP in the absence of ST.

Films were submitted to FTIR analysis, CI was calculated by eq. (1), and the calibration curve was constructed, as shown in Figure 1.

#### Calibration curve of the MA and ST amounts in PP

Known amounts of PP and MAST were mixed in the Haake rheometer. Care was taken to submit MAST to thermal treatment in a vacuum oven at 90°C for 21 h before processing to convert possible acid groups of the succinic units to anhydrides.

The concentrations of MAST in PP were 0.5, 1, 3, and 4 wt %. According to the MAST1000 manufacturer (Elf Atochen), this copolymer was 1 : 1 molar ST–MA.

Infrared spectra were obtained under the same conditions as the MA and ST grafted PP samples.

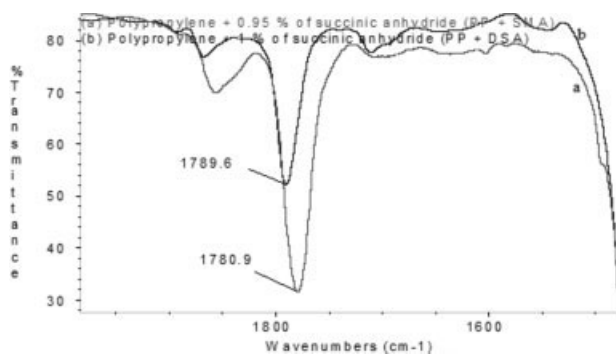
CI was calculated from the infrared spectra with eq. (2).

Although blends were processed in the rheometer with known amounts of MAST and PP and the SMA monomer molar ratio was supplied by the manufacturer, titration was performed to confirm the anhydride amount in the blend.

#### Titration of MA acid groups

Titration requires all succinic groups be converted from anhydrides to acids. The methodology used was based on investigations by Gaylord and Mishra<sup>1</sup> and is described as follows. One gram of a certain PP–MAST blend, obtained in the torque rheometer, was dissolved in 150 mL of xylene at 120°C with refluxing. After complete dissolution, 200 μL of distilled water was added, and the solution remained under refluxing for an additional hour for complete hydrolysis of the succinic groups.

Afterward, the solution was titrated at 90°C with 0.05N ethanolic KOH, with phenolphthalein as an



**Figure 2** FTIR spectra of (a) PP + MAST (SMA 1000) and (b) PP + DSA.

indicator. Excess base was added, and the solution was back-titrated with 0.05N isopropanolic HCl.

**RESULTS AND DISCUSSION**

**Calibration curves**

The need to construct calibration curves arises from the fact that CI measurements are relative measurements. To obtain the absolute amounts of grafted MA and ST, such curves were required.

A calibration curve for MA grafting, in the absence of ST, was already constructed for the investigated systems in previous studies<sup>2-4</sup> by the blending of PP and DSA. Regression analysis allowed us to obtain a curve with correlation index of 0.99986:

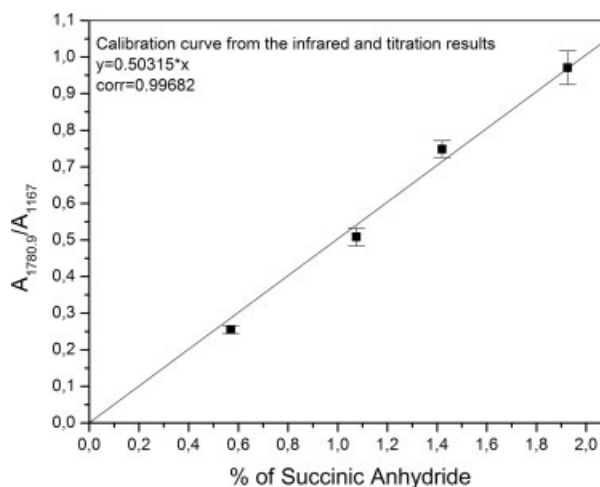
$$y = 0.1790 \times x \tag{4}$$

where  $y = A_{1789.6}/A_{1167}$ , that is, the carbonyl index of maleic anhydride ( $CI_{MA}$ ), and  $x$  is the percentage of succinic anhydride present.

However, the analysis of the results of the MA grafting onto PP in the presence of ST showed a shift in the carbonyl band from 1789.6  $cm^{-1}$  when ST was absent to 1780.9  $cm^{-1}$  when ST was present. Also, on application of the PP-MA system calibration curve equation, the absolute values obtained of %MA<sub>r</sub> exceeded the amount of MA added to the system. The two absorption band intensities were different

**TABLE III**  
Theoretical Data of the Percentage MA and the Average Results of the FTIR Measurements and Standard PP and MAST Sample Titrations

	Theoretical added MA (%)	MA obtained by titration (%)	$CI_{MA-ST} = A_{1780.9}/A_{1167}$
1	0.486	0.57	0.25475
2	0.969	1.075	0.50873
3	1.455	1.42	0.74869
4	1.94	1.925	0.97078



**Figure 3** Calibration curve of %MA<sub>r</sub> (succinic anhydride) in PP in the presence of ST from the FTIR and titration results.

for the same anhydride amounts present because the anhydride neighbors changed. It was, therefore, necessary to construct a new calibration curve to quantify the 1780.9- $cm^{-1}$  carbonyl. A new calibration curve was constructed from known amounts of PP and SMA1000, a commercial 1 : 1 molar ratio of ST-MA in the copolymer.

The infrared spectra curves of the standard PP + DSA with the carbonyl band at 1789.6  $cm^{-1}$  and PP + MAST with the carbonyl band at 1780.9  $cm^{-1}$  with approximately the same amounts of succinic anhydride present (1 wt %) are shown in Figure 2. As shown in this figure, there was a shift of the carbonyl band where MA was attached to ST and a difference in the peak intensity for the same amounts of MA present.

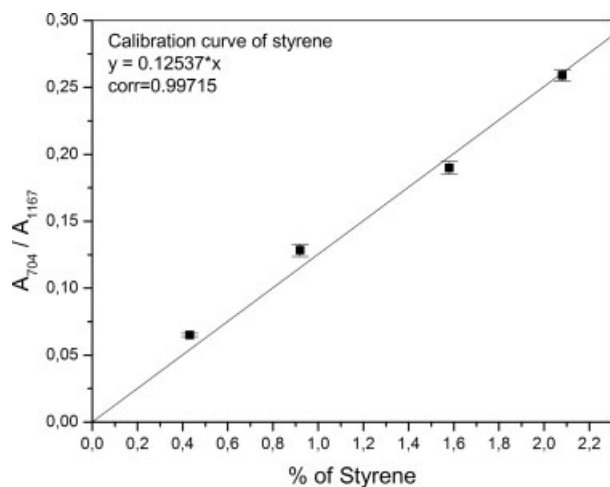
Titrations were performed to confirm the 1 : 1 molar ratio between the MAST monomers, and the results are shown in Table III.

From the infrared and titration results, a calibration curve was constructed to quantify succinic anhydride in the samples processed with PP, MA, ST, and peroxide. The following equation obtained presented a correlation coefficient of 0.99682:

$$y = 0.50315 \times x \tag{5}$$

**TABLE IV**  
Values of Percentage ST Present and Average FTIR Results of the Standard PP and SMA Samples

	Theoretical ST added (%)	Relative amount of ST = $A_{704}/A_{1167}$
1	0.432	0.06501
2	0.92	0.12833
3	1.58	0.18985
4	2.08	0.25902



**Figure 4** Calibration curve for ST quantification from the FTIR measurements.

where  $y = A_{1780.9}/A_{1167}$ , that is, the carbonyl index of maleic anhydride–styrene ( $CI_{MA-ST}$ ), and  $x$  is the percentage of succinic anhydride present.

The calibration curve of %MA<sub>r</sub> (succinic anhydride) in PP in the presence of ST is shown in Figure 3.

ST content in the standard samples was calculated from the titration data of the standards and the

amounts of MAST(SMA 1000) added to the PP–MAST blends. Table IV lists the average values of percentage ST in the PP–MAST blends and respective absorbance values.

The calibration curve used to quantify ST by FTIR (Fig. 4) was constructed from the data in Table IV. A fit of the data allowed us to obtain eq. (6) with a correlation coefficient of 0.99715:

$$y = 0.12537 \times x \quad (6)$$

where  $y = A_{704}/A_{1167}$  and  $x$  is the weight percentage of styrene.

#### Effect of the independent variables on %MA<sub>r</sub> and percentage reacted styrene and on the MFI

The results of FTIR analysis, the quantification of reacted MA and ST, and MFI are shown in Tables V and VI, respectively.

Multiple-regression analyses performed by statistical computer programs allowed us to fit the results of %MA<sub>r</sub> and %ST<sub>r</sub> by second-order models and MFI results by third-order models. The coefficients of the fitted polynomial equations are listed in Table VII.

**TABLE V**  
FTIR Results and %MA<sub>r</sub> and %ST<sub>r</sub> in the Samples Submitted to Reactive Processing in the Haake Torque Rheometer

Run	Variable			Response					
	C <sub>MA</sub> (phr)	C <sub>ST</sub> (phr)	C <sub>PER</sub> (phr)	CI = A <sub>1780.9</sub> /A <sub>1167</sub>	%MA <sub>r</sub>	Average %MA <sub>r</sub>	A <sub>704</sub> /A <sub>1167</sub>	%ST <sub>r</sub>	Average %ST <sub>r</sub>
H01									
a	1.5	1.5	0.1	0.29511	0.587	0.609	0.10014	0.799	0.782
b	1.5	1.5	0.1	0.31726	0.631		0.09573	0.764	
H02									
a	6.5	1.5	0.1	0.41831	0.831	0.725	0.08189	0.653	0.578
b	6.5	1.5	0.1	0.31078	0.618		0.06299	0.502	
H03									
a	1.5	6.5	0.1	0.22989	0.457	0.449	0.15470	1.234	1.404
b	1.5	6.5	0.1	0.22212	0.441		0.19717	1.573	
H04									
a	6.5	6.5	0.1	0.80335	1.597	1.471	0.17996	1.435	1.351
b	6.5	6.5	0.1	0.67603	1.344		0.15869	1.266	
H05									
a	4.0	4.0	0.1	0.66599	1.324	1.289	0.17421	1.390	1.295
b	4.0	4.0	0.1	0.63065	1.253		0.15028	1.199	
H06									
a	4.0	4.0	0.1	0.61594	1.224	1.303	0.15970	1.274	1.316
b	4.0	4.0	0.1	0.69547	1.382		0.17012	1.357	
H07									
a	0.5	4.0	0.1	0.10535	0.209	0.250	0.13691	1.092	1.141
b	0.5	4.0	0.1	0.14590	0.290		0.14912	1.189	
H08									
a	7.5	4.0	0.1	0.61323	1.219	1.173	0.12891	1.028	0.965
b	7.5	4.0	0.1	0.56692	1.127		0.11251	0.897	
H09									
a	4.0	0.5	0.1	0.38770	0.771	0.656	0.06326	0.505	0.452
b	4.0	0.5	0.1	0.27165	0.540		0.05001	0.399	
H10									
a	4.0	7.5	0.1	0.79728	1.585	1.424	0.26272	2.096	1.950
b	4.0	7.5	0.1	0.63572	1.263		0.22620	1.804	

**TABLE VI**  
MFI Results of the Samples Submitted to Reactive Processing in the Haake Torque Rheometer

Run	Variable			Response	
	C <sub>MA</sub> (phr)	C <sub>ST</sub> (phr)	C <sub>PER</sub> (phr)	MFI	Average MFI
H01					
a	1.5	1.5	0.1	9.05	8.87
b	1.5	1.5	0.1	8.68	
H02					
a	6.5	1.5	0.1	25.37	25.92
b	6.5	1.5	0.1	26.47	
H03					
a	1.5	6.5	0.1	4.17	4.10
b	1.5	6.5	0.1	4.02	
H04					
a	6.5	6.5	0.1	10.67	10.00
b	6.5	6.5	0.1	9.32	
H05					
a	4.0	4.0	0.1	11.19	11.34
b	4.0	4.0	0.1	11.49	
H06					
a	4.0	4.0	0.1	12.50	10.89
b	4.0	4.0	0.1	9.28	
H07					
a	0.5	4.0	0.1	4.03	4.44
b	0.5	4.0	0.1	4.84	
H08					
a	7.5	4.0	0.1	30.38	30.85
b	7.5	4.0	0.1	31.32	
H09					
a	4.0	0.5	0.1	69.02	58.43
b	4.0	0.5	0.1	47.83	
H10					
a	4.0	7.5	0.1	8.26	6.26
b	4.0	7.5	0.1	4.26	

Analysis of the effect of each independent variable by plain observation of the fitted equations that correlated them with the dependent variable (%MA<sub>r</sub> or %ST<sub>r</sub>) was not easy. It became, therefore, necessary to construct surface response graphs from the proposed equations. The experimental design graphs (the reactions of MA grafting onto PP in the presence of ST) are shown later in Figures 7, 10, and 11.

To assess the effect of the presence of one of the monomers on the reactivity of the other, reactive processing was performed with only one of the monomers (references) under the same concentrations as those used in the reactive processing in the pres-

ence of the two monomers. The responses are shown in Table VIII.

Figures 5 and 6 show graphs of %MA<sub>r</sub> and A<sub>700</sub>/A<sub>1167</sub> versus added C<sub>MA</sub> and C<sub>ST</sub>, respectively, without comonomer addition.

The calibration curve used to quantify %ST<sub>r</sub> was not used when processing was done in the absence of MA, as the ST absorption band occurred at 700 cm<sup>-1</sup>, whereas in the presence of MA, this band occurred at 704 cm<sup>-1</sup>. Hence, to avoid possible errors in ST quantification (as the calibration curve was constructed in the presence of MA), Table VIII and Figure 6 present only the ratio between the 700 and 1167 absorption bands, which was a relative measurement of %ST<sub>r</sub>.

For analysis, the values of %MA<sub>r</sub> in the samples processed in the torque rheometer containing only MA monomer were compared with those containing both monomers (MA and ST) for the same initial C<sub>MA</sub> values. The comparisons of %MA<sub>r</sub> in Tables V and VIII and Figures 5 and 7 show that the presence of ST in the reaction medium increased the reactivity of MA only when it was added at the same concentration as MA (equimolar ratios) or when the total concentration of added monomers exceeded 10 phr. Moreover, this effect was only seen when MA exceeded 4 phr. Hu et al.<sup>14,15</sup> observed an increase in %MA<sub>r</sub> in the presence of ST at all investigated concentrations when MA and ST were incorporated at equimolar ratios. However, the amount of peroxide used in their investigations was five times higher than that used in our investigation.

On assessment of the effect of the presence of ST in the PP-MA and peroxide reactive blend on MFI values showed a decrease for all formulations containing ST (Table VI) when compared with the values of those having equal C<sub>MA</sub> values but without ST (Table VIII). Because MFI is a relative measure of polymer molecular weight, we can state that less degradation occurred in the presence of ST. This behavior might be explained by the fact that when ST was introduced into a reaction mixture, it reacted with the active centers of the polymeric macroradicals and, hence, minimized the occurrence of β scission and, consequently, reduced PP degradation. Increasing the overall monomer concentration (MA and ST) in the

**TABLE VII**  
Coefficients of the Fitted Polynomials for Surface Response Construction

	R <sup>2</sup>	Linear terms			Quadratic terms			Cubic terms	
		a <sub>0</sub>	a <sub>1</sub>	a <sub>2</sub>	a <sub>3</sub>	a <sub>4</sub>	a <sub>5</sub>	a <sub>6</sub>	a <sub>7</sub>
%MA <sub>r</sub>	95.5	-0.10385832	0.37135472	0.12262864	0.03621056	-0.04925552	-0.02297536	—	—
%ST <sub>r</sub>	87.4	0.2119394	0.1513472	0.1756828	—	-0.0189184	—	—	—
MFI	80.5	44.56341572	15.00220109	-35.29921613	—	-3.750550272	7.642312032	0.312545856	-0.538318336

Polynomial equation:  $a_0 + a_1C_{MA} + a_2C_{ST} + a_3C_{MA}C_{ST} + a_4C_{MA}^2 + a_5C_{ST}^2 + a_6C_{MA}^3 + a_7C_{ST}^3$ .

TABLE VIII  
Reference Formulations Processed in the Haake Torque Rheometer

Run	$C_{PER}$ (phr)	$C_{MA}$ (phr)	$C_{ST}$ (phr)	%MA <sub>r</sub>	$A_{700}/A_{1167}$	MFI (g/10 min)
11	0	0	0	0	0	2.51
12	0.1	0	0	0	0	47.57
13	0.1	0.5	0	0.434	0	78.105
14	0.1	1.5	0	0.648	0	89.87
15	0.1	4.0	0	0.700	0	71.185
16	0.1	6.5	0	0.623	0	53.68
17	0.1	7.5	0	0.538	0	43.925
18	0.1	0	0.5	0	0.06611	7.195
19	0.1	0	1.5	0	0.08854	6.58
20	0.1	0	4.0	0	0.13020	5.545
21	0.1	0	6.5	0	0.13876	4.875
22	0.1	0	7.5	0	0.15030	4.665

reaction mixture increased the probability that the monomers would be close to a reactive center formed in the PP. Moreover, increasing MA reactivity in relation to PP decreased the reactive centers in PP that were responsible for chain scission.

As to ST, a quantitative analysis could not be performed because it was not possible to construct a calibration curve for the reaction of ST with PP in the absence of MA. However, a comparison of the curves in Figures 6 and 11 (shown later) revealed that the effect of  $C_{ST}$  on the %ST<sub>r</sub> response had the same behavior in the absence and presence of MA.

After analyzing the effect of ST presence on %MA<sub>r</sub>, MFI, and %ST<sub>r</sub>, we assessed the effect of each independent variable ( $C_{MA}$  and  $C_{ST}$ ) on the investigated responses.

As shown in Figure 7, an increase in initial  $C_{MA}$  led to two distinct types of behavior depending on  $C_{ST}$ . For low initial  $C_{ST}$  values, an increase in  $C_{MA}$  in the reaction medium resulted in an increase in %MA<sub>r</sub> up to a maximum, when  $C_{MA}$  reached 4 phr; %MA<sub>r</sub> then decreased for higher  $C_{MA}$ . This behavior was similar to that shown by the increase in  $C_{MA}$  in the absence of ST (Fig. 5). This behavior indicated that above 4 phr, it was likely that two PP-MA phases were

formed in virtue of low MA solubility in PP. For  $C_{ST}$  values equal to or exceeding 4 phr, an increase in  $C_{MA}$  resulted in an increase in %MA<sub>r</sub>. At this point, a change in the response of %MA<sub>r</sub> was seen when compared to the reaction in the absence of ST.

According to Odian,<sup>20</sup> MA has little tendency to homopolymerize but easily forms an alternating copolymer with electron-donating monomers, such as ST. The  $r_1$  and  $r_2$  (monomer reactivity ratios) values for MA and ST monomers (in the presence of one another) are 0.005 and 0.050, respectively. The tendency to alternate depends on the temperature and total monomer concentration. Alternation decreases with increases in temperature and with reductions in total monomer concentration because the extent of complex formation decreases. This fact explains the increase in %MA<sub>r</sub> compared to the same  $C_{MA}$  in the system without ST at high total monomer concentrations (above 10 phr), even without equimolar ratios.

The formation of MAST branches on the PP backbone was evidenced by the shift of the cyclic anhydride carbonyl band from 1789.6 cm<sup>-1</sup> (for the reactive processing of PP and MA) to 1780.9 cm<sup>-1</sup> (for the reactive processing of PP, MA, and ST). Figure 8

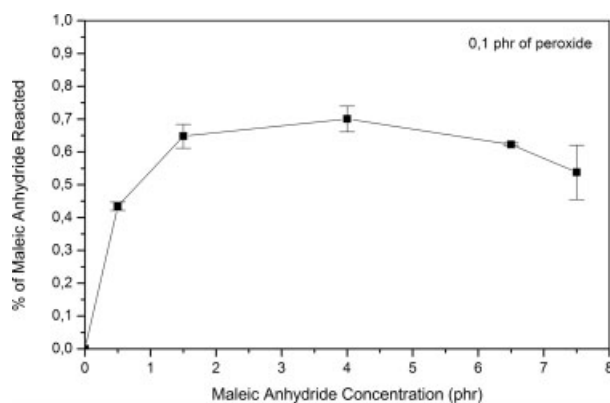


Figure 5 Effect of initial  $C_{MA}$  on %MA<sub>r</sub> (with MA as only monomer in the reaction).

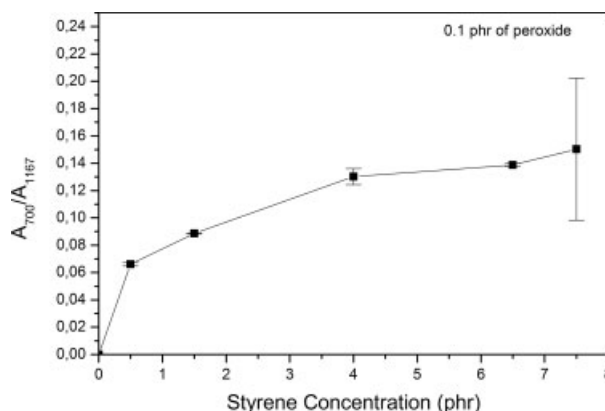
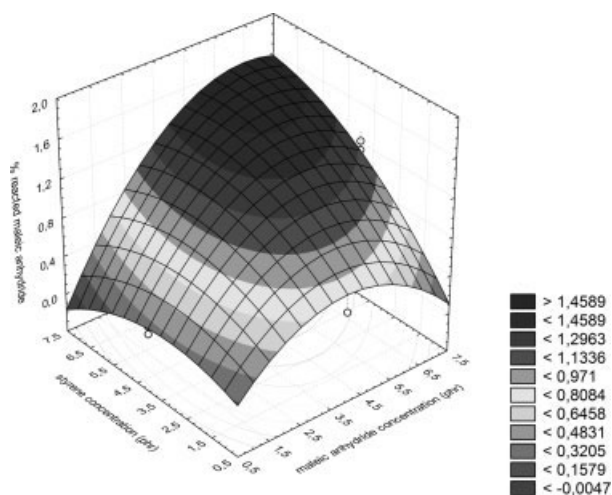
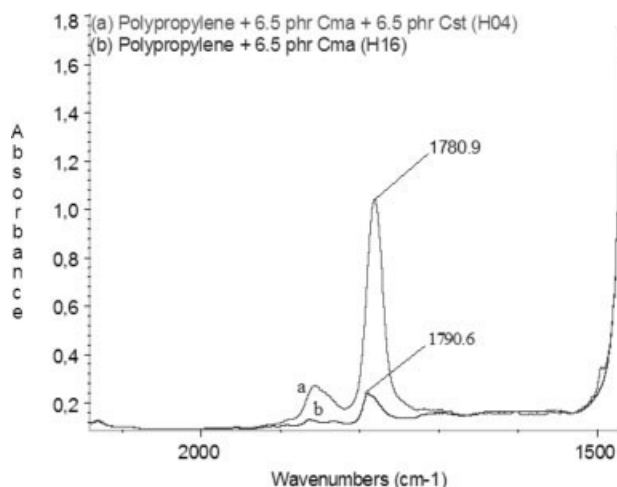


Figure 6 Effect of initial  $C_{ST}$  on the absorbance ratio between 700 and 1167 cm<sup>-1</sup>, a relative measure of %ST<sub>r</sub> (with ST as only monomer).

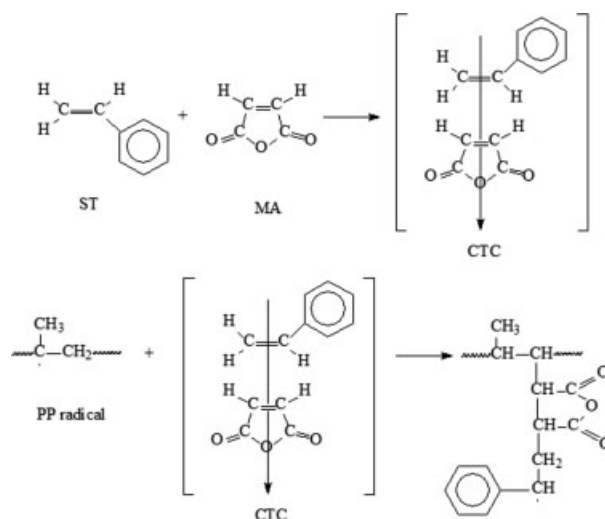


**Figure 7** Effect of  $C_{MA}$  and  $C_{ST}$  on  $\%MA_r$  during reactive processing (experimental design).

shows the FTIR spectra of samples H04 (PP + 6.5 phr  $C_{MA}$  + 6.5 phr  $C_{ST}$ ) with the cyclic anhydride carbonyl absorption at  $1780.9\text{ cm}^{-1}$  and of sample H16 (PP + 6.5 phr de  $C_{MA}$ ) with carbonyl absorption at  $1789.6\text{ cm}^{-1}$ . To plot the reactive processing calibration curves, DSA, with absorption at  $1790\text{ cm}^{-1}$ , and a 1 : 1 molar MAST, with absorption at  $1780.9\text{ cm}^{-1}$ , were used. The coincidence of carbonyl anhydride at  $1780.9\text{ cm}^{-1}$  was a strong indication of alternating copolymerization of MA and ST. These assumptions could only be made because of the purifications performed with the materials obtained during reactive processing of PP, MA, ST, and peroxide. During solubilization in xylene and precipitation in acetone, residual monomers, unreacted MA oligomers, and unreacted MAST were dissolved in acetone, whereas PP-g-MA, PP-g-MAST, PP-g-ST, and PP precipitated in it. Therefore, MAST in the precipitate was likely bonded to PP and not just mixed in the reaction mass.



**Figure 8** FTIR spectra of samples (a) H04 (PP + 6.5 phr  $C_{MA}$  + 6.5 phr  $C_{ST}$ ) and (b) H16 (PP + 6.5 phr  $C_{MA}$ ).

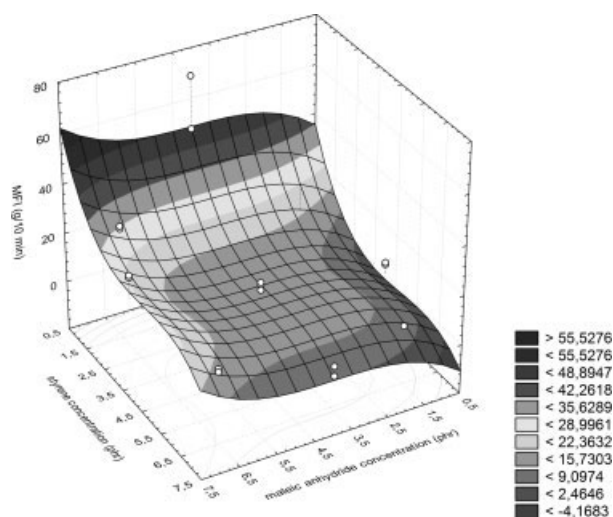


**Figure 9** Reaction scheme proposed for the copolymerization of MA and ST onto PP, according to Hu et al.<sup>14,15</sup>

Although the calibration curve of PP + MAST was constructed with a blend of these components, that is, with no appreciable bonding between these, this curve could be used to obtain the absorption band of succinic anhydride when bonded to ST.

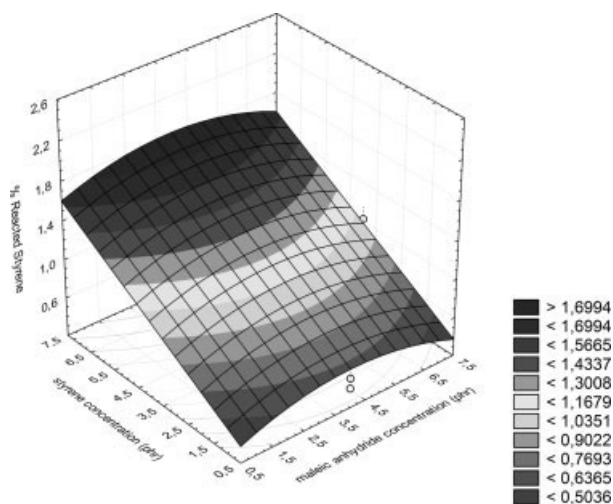
The results indicate that in the presence of ST, MA likely activated the reactivity of the double bond to form a CTC,<sup>16,18</sup> which increased  $\%MA_r$  and formed branches of an alternating MAST on PP. Similar results were presented by Li et al.<sup>21</sup> The reaction scheme, presented by Hu et al.,<sup>14</sup> is shown in Figure 9.

Therefore, the increase in  $\%MA_r$  in PP indicated that the reactivity of MA in relation to PP was not the only event that might have occurred. The increase in  $\%MA_r$  may also have arisen from a higher amount of anhydride as a comonomer of a MAST branch.



**Figure 10** Effect of  $C_{MA}$  and  $C_{ST}$  on MFIs of the samples processed in the Haake torque rheometer (experimental design).





**Figure 11** Effect of  $C_{MA}$  and  $C_{ST}$  on  $\%ST_r$  during reactive processing (experimental design).

Having analyzed the effect of ST presence and  $C_{MA}$  and  $C_{ST}$  on  $\%MA_r$ , we then analyzed MFI, which is a relative measure of polymer molecular weight.

Figure 10 shows the analysis of MFI as a function of  $C_{MA}$  and  $C_{ST}$ . An increase in  $C_{ST}$  was shown to reduce MFI; that is, it reduced PP degradation as a consequence of the increasing probability that ST monomers became available for reaction with the polymer macroradicals, which hence minimized chain scission, which occurred in the absence of a reaction with any one of the monomers. Moreover, the reaction of ST with MA prevented MA termination by chain transfer with PP, which would have led to the formation of more polymer macroradicals and hence increased the probability of chain scission.

As to the effect of  $C_{MA}$  on MFI, a slight increase was seen at low  $C_{MA}$  values, followed by a long region of practically constant MFIs and a small increase at very high  $C_{MA}$ . This behavior seemed to indicate a limiting  $C_{MA}$  that reacted with PP. It was no use to exceed this value, for MFI did not decrease. However, as ST likely reacted with MA, termination by chain transfer was impaired, which minimized possible chain scission that would have occurred in the absence of ST. The MFI increase at low  $C_{MA}$  and/or  $C_{ST}$  values likely occurred because of chain-transfer reactions with PP because, as explained before, at MA-ST ratios below equimolar or even at low overall monomer concentrations, the formation of the charge complex and, consequently, of the alternating MAST copolymer was reduced.

As to the  $\%ST_r$  response, Figure 11 shows that an increase in  $C_{ST}$  present in the initial reaction led to an increase in  $\%ST_r$ . Therefore, the higher the amount of ST monomer present in the reaction mixture, the higher the probability it would be present at the formed reactive centers, in PP and in MA, and hence, more ST reacted in the modified polymer.

An increase in  $C_{MA}$ , however, did not lead to pronounced variations in  $\%ST_r$ , yet an increase of this response was seen up to a maximum, after which  $\%ST_r$  dropped. This behavior showed that the formation of the CTC was a factor that markedly affected MA reactivity but not that of ST.

## CONCLUSIONS

Reactive processing in a Haake torque rheometer was shown to be effective in the promotion of the grafting of MA and ST onto PP.

The presence of ST monomer in the grafting reaction of MA onto PP significantly increased  $\%MA_r$ , when this was added at equimolar ratios or when the overall monomer concentrations were high. The presence of ST and the increase in its initial concentration in the monomer blend reduced PP degradation, as evidenced by the decrease in MFI.

$C_{MA}$  had a significant effect on  $\%MA_r$ , both in the absence and in the presence of ST; however, this behavior was different in both cases. When ST was present, there was evidence of alternate ramification formation of MA and ST in the PP.

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