

Bulk Modification of Styrene–Butadiene–Styrene Triblock Copolymer with Maleic Anhydride

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ABSTRACT: The bulk modification of SBS rubber with maleic anhydride in a mixing chamber of a Haake rheomixer was studied. The effect of temperature, maleic anhydride, and benzoyl peroxide concentrations on the grafting efficiency was evaluated. High grafting efficiency was achieved when the ratio of peroxide and maleic anhydride concentration was high. On the other hand, on this condition high insoluble fraction was generated. The addition of a diamine, 4,4'-diaminodiphenylmethane to the reaction mixture minimizes the amount of insoluble polymer. However, the grafted MAH content also decreases. The graft copolymer was characterized by infrared spectroscopy and the grafting extension was determined by titration. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2953–2960, 2002; DOI 10.1002/app.10355

Key words: block copolymers; functionalization of polymers; reactive processing

INTRODUCTION

In the last decades academic and industrial interest in chemical modification of polymers has increased. Normally the chemical modification of polymers improves the original adhesion to a substrate and the reactivity.

Maleic anhydride (MAH) has been the more commonly used molecule for functionalization of polymers due to the facility of the grafting in the normal melt processing temperature of the polymers and to the high reactivity of the anhydride group in successive reactions. The MAH grafting reaction can be conducted in polymer solution^{1–3} or in the melt state.^{4–6} For the grafting of MAH a number of reactions have been proposed. The initiation of the grafting involves radicals originated

from peroxide decomposition or from thermal and mechanical processes. The radicals abstract hydrogen from the polymer chain,⁷ resulting in macroradicals. MAH molecules add to these macroradicals forming MAH radicals covalently bonded to the polymer. The polymer-grafted MAH (*g*-MAH) radicals have a low tendency to homopolymerize, and the radical is transferred to an adjacent polymer chain.

MAH has been grafted onto SEBS,^{8,9} poly-*cis*-butadiene,¹⁰ styrene–isoprene block copolymers,¹ EPDM,^{4,6,11} EPR,^{2,12} and others.

Gaylord et al.² studied the grafting of MAH onto EPR rubber in the melt in the presence of high MAH concentrations, using a Brabender mixer. The grafting reaction under conditions at which peroxides have short half-lives time results in the formation of excited reactive MAH species. These excited MAH species increase the radical generation on the polymer; therefore, grafting reaction, crosslinking, or chain scission can take place.

Gaymans and Oostenbrink⁴ showed that functionalization of EPDM rubber by grafting with

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Table I Properties of the SBS Used in This Study

	\bar{M}_w^a (g/mol)	\bar{M}_w/\bar{M}_n^a	Composition wt % ^b	Melt Flow Index (g/10 min) ^c	Source
SBS	105000	1.1	Styrene: 66 Cis-1,4-butadiene: 12 Trans-1,4-butadiene: 18 Vinyl-1,2-butadiene: 4	4.4	COPERBO

^a Determined by gel permeation chromatography.

^b Determined by ¹³C-NMR.

^c Provided by manufacturer.

MAH in a twin-screw extruder is possible. It was observed that the reaction occurs in the presence and in the absence of an initiator, but it is more efficient in the first case. The MAH solubility in the EPDM matrix has an important role in the grafting efficiency. When the MAH concentration exceeds the solubility limit, the amount of *g*-MAH decreases.

Styrene-butadiene-styrene triblock copolymers (SBS) are an important class of thermoplastic elastomers. They behave as vulcanized rubbers at room temperature, and yet can be processed as thermoplastics at elevated temperatures. The anionic polymerization technique employed to synthesize these block polymers is not appropriate to incorporate some polar monomers in the polymer chain. Under these circumstances, chemical modification to generate polar groups on the polymer appears to be a viable approach. The epoxidation method in solution and in the solid state has been widely used for the chemical modification of SBS.¹³⁻¹⁶

MAH groups introduced onto SBS can increase its polarity and compatibility with polar polymers. The grafting reaction of MAH onto SBS in solution and the properties of the grafted-SBS adhesive were studied by Zhu et al.³

This article describes the modification of SBS rubber with MAH in the melt, using a Haake rheomixer as the reactor. The influence of temperature, benzoyl peroxide, and maleic anhydride concentrations on the grafting reaction was analyzed. The reaction was conducted in the absence as well as in the presence of a diamine (4,4'-diaminediphenylmethane).

EXPERIMENTAL

Materials

All the materials were used without further purification. The styrene-butadiene-styrene triblock

copolymer (SBS) was supplied by Coperbo Petroflex Ind. and Com. S.A. (TR-1061). Selected characteristics of the SBS rubber are gathered in Table I. The benzoyl peroxide (BP), Aldrich—97% purity, maleic anhydride (MAH), Elekeiroz—95% purity, and 4,4'-diaminediphenylmethane, Bayer S.A., were used.

Reaction Procedure

Forty-four grams of SBS rubber were premixed with MAH and benzoyl peroxide then charged into a preheated Haake Rheomixer Model 600. In Table II are shown the MAH and peroxide concentrations and the temperatures used. All experiments were performed at 55 rpm for 20 min. Torque-temperature curves were automatically recorded during the experiment.

The MAH grafting reaction onto SBS was also conducted in the presence of a diamine (4,4'-diaminediphenylmethane). The mixture of MAH, peroxide, and diamine was added after 240 s to the molten SBS in the mixer chamber at 150°C and 55 rpm. For these experiments the MAH and peroxide concentrations were fixed in 12 and 0.2 wt %, respectively. The diamine concentrations are showed in Table III. To some samples more diamine was added after approximately 780 s of mixing. The reaction product was removed from the chamber mixer after a 20-min mixture. The samples obtained in the presence of diamine were named 12SBS_{*n*}, where 12 correspond to the MAH concentration and the subscript *n* to the number of the experiment.

Characterization

The modified SBS obtained in the absence of diamine exhibiting a fraction of insoluble chains were dried in a vacuum oven at 120°C for 20 h to sublimate the free and unreacted maleic anhydride. The efficiency of this method was confirmed by thermogravimetry.¹⁷

Table II Reactions Conditions, Grafted MAH Contents, Grafting Efficiency, Insoluble Fraction of Modified SBS, and Torque at 400 s of Reaction

Temperature (°C)	Peroxide ^a wt %	MAH ^b wt %	Grafted MAH wt %	Grafting Efficiency (%)	Insoluble Fraction (%)	Torque ^c g	\bar{M}_w ^d g/mol	\bar{M}_w/\bar{M}_n ^d
130	0	0	0	0	0	1300	—	—
		6	0	0	0	1186	—	—
		8	0	0	0	1200	—	—
		10	0	0	0	981	—	—
		4	2.1	50	80	1300	—	—
	0.1	6	1.9	32	76	1500	—	—
		12	1.3	11	47	1404	—	—
		0	0	0	0	1200	—	—
		10	3.0	30	77	1743	—	—
		12	1.7	14	71	1662	—	—
	0.2	20	1.3	7	63	935	—	—
		25	1.1	4	40	760	—	—
		12	2.1	18	91	1458	—	—
		0.0	0	0	0	900	97,000	1.3
		0.2	0	0	0	880	127,000	1.7
150	0.2	8	3.3	41	78	1295	—	—
		13	3.0	23	79	1564	—	—
		15	2.3	15	60	942	—	—
		25	1.2	5	41	858	—	—
		0.0	0	0	0	570	—	—
170	0.2	0	0	0	410	—	—	
	0.2	10	1.9	19	73	1261	—	—

^a In relation to total mixture.

^b In relation to SBS weight.

^c Torque at 400 s reaction.

^d Determined by gel permeation chromatography.

The soluble-modified SBS was purified by dissolution in toluene at room temperature and further precipitation in methanol to remove free diamine and MAH. This procedure was repeated three times. The polymer was dried in a vacuum oven at 65°C for 9 h.

FTIR spectra by ATR or transmittance of the modified SBS were recorded on a Perkin-Elmer FTIR Spectrometer 1600 series from 400 cm⁻¹ to 4000 cm⁻¹ at a resolution of 2 cm⁻¹ and 20 scans. The reaction product obtained in the absence of diamine was analyzed by ATR and the product

Table III Molar Ratio of Diamine and Anhydride Used to the MAH Grafting on SBS.

Samples	Diamine/Anhydride (mol %)			Torque (g)		Grafted MAH (%)	Grafting Efficiency (%)	\bar{M}_w ^a g/mol	\bar{M}_w/\bar{M}_n ^a
	After 240 s	After 720 s	Total	After 480 s	After 1140 s				
12SBS ₁	0.415	0.855	1.27	197	1800	—	—	∞	—
12SBS ₂	0.176	0.855	1.03	479	993	—	—	∞	—
12SBS ₃	0.096	0.184	0.28	857	644	0.26	2.5	121000	1.2
12SBS ₄	0.085	0	0.085	877	595	0.33	2.5	107000	1.1
12SBS ₅	0.043	0	0.043	1081	1159	0.20	1.7	119000	1.2

Reactions conditions: 12 wt % of MAH, 0.2 wt % of benzoyl peroxide, temperature of 150°C, 55 rpm.

obtained in the presence of diamine by transmission technique. For ATR analyses the films used were obtained by compression of the purified reaction products under 2 MPa pressure at 150°C for 2 min. For transmission analyses, films of the purified reaction products were obtained by casting from CH₂Cl₂ solution on KBr crystals.

The grafted anhydride concentration in the purified products was determined by titration of the acid group derived from the anhydride function. After dissolution or dispersion of 1 g of SBS-*g*-MAH in 50 mL of toluene under reflux, 200 μL of water were added to hydrolyze the anhydride. The reflux was maintained for 1 h. The hot solution was titrated with 0.025 M potassium hydroxide in methanol/benzyl alcohol 1/9 (v/v) using phenolphthalein (1% in methanol) as the indicator. The KOH solution was standardized against a solution of potassium hydrogen phthalate.

The insoluble fraction of the modified SBS was determined by extraction of soluble fraction with an appropriate solvent. The reaction products obtained in the absence of diamine were stirred with toluene for a week. The solvent was changed during the first 2 days. The insoluble fraction was separated by filtering the suspension, dried in a vacuum oven at 65°C for 12 h, and weighed to obtain the amount of insoluble rubber content.

The molecular weight of the SBS and modified SBS was determined using a Waters 150 CV-Gel Permeation Chromatograph with THF as solvent and μ-styragel columns. Calibration was performed using polystyrene standards.

RESULTS AND DISCUSSION

Figure 1 shows the torque of pure SBS during the mechanical processing at 150°C and 55 rpm in the absence and in the presence of peroxide and MAH. The torque of the pure SBS varies slightly, while in the presence of benzoyl peroxide it decreases gradually with time. Similar results were obtained at other temperatures; however, the torque drop is more pronounced as the processing temperature increases. Table II shows the torque of the reactions mixture at 400 s of processing in the presence and in the absence of peroxide at different temperatures and the molecular weight and the molecular weight distribution for samples processed at 150°C. The average molecular weight of SBS decreases, while the molecular weight distribution increases. Therefore, the decrease of torque is associated to the decrease of

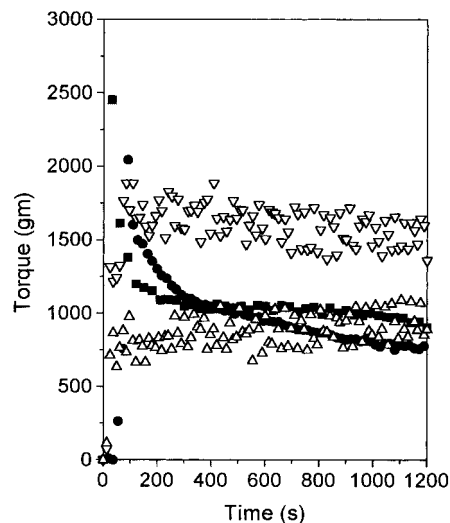


Figure 1 Torque as a function of time: pure SBS (■) and mixtures of SBS, 0.2 wt % of benzoyl peroxide and 0 (●), 13 (▽) and 25 wt % of MAH and (△). Processing conditions: 150°C, 55 rpm for 20 min.

the molecular weight of SBS, which is more pronounced in the presence of peroxide and at a higher processing temperature.

When MAH is added to SBS and peroxide mixture the torque oscillates strongly (Fig. 1). However, the observed tendency of the torque is to become lower and higher than of the SBS processed in the presence of peroxide, for SBS modified in the presence of 25 and 13 wt % of MAH, respectively. This behavior suggests a plasticizer effect of free anhydride on the SBS. This hypothesis is reinforced by the results obtained for SBS processed only in the presence of MAH (Table II, experiment conducted at 130°C, 0 wt % of peroxide and variable concentration of MAH). At these conditions no grafting took place, and the increase of MAH concentration resulted in a decrease of torque. There is no evidence of phase segregation at higher MAH concentration.

The torque value at 400 s of the reaction mixtures containing 0.2 wt % of benzoyl peroxide at 150°C is plotted as a function of MAH weight percentage in Figure 2. The torque of the SBS/MAH/BP mixtures increases for MAH concentration up to 13 wt % and then decreases and reaches smaller values than that for pure SBS. The same behavior was observed at other peroxide concentration (0.1 and 0.3 wt %) and other processing temperatures (130 and 170°C).

The grafted MAH content in the modified SBS as well as the efficiency of grafting, insoluble frac-

tion, and the torque at 400 s reaction are showed in Table II. The grafted MAH content determined by titration is expressed as the weight fraction of MAH in the modified SBS. The efficiency of grafting is defined as the ratio of MAN content in the modified SBS and MAH concentration used for the modification, expressed as percentage. The grafting efficiency and the insoluble fraction decrease as the MAH concentration increases independent of peroxide concentration and temperature (Fig. 3). The grafting efficiency also depends on the molar ratio of peroxide and anhydride ($[\text{peroxide}]/[\text{MAH}]$) and on the temperature as shown in Figure 4(a). The increase of this ratio at constant temperature results in a higher grafting degree and in an insoluble fraction. The insoluble fraction presents no dependence on the temperature, at least in the temperature range studied [Fig. 4(b)].

This behavior can be explained by a mechanism for MAH grafting based on the occurrence of MAH excited species (excimer) in the reaction medium.^{5,6,19,20} The higher the $[\text{peroxide}]/[\text{MAH}]$ ratio, the higher the MAH excited species concentration and, consequently, the higher the grafting and crosslinking degree obtained. The highest grafting degree was obtained at 150°C.

The FTIR spectra of pure SBS and grafted-SBS modified in the presence of benzoyl peroxide, after removal of free MAH, are shown in Figure 5. The FTIR spectrum of grafted copolymer presents a new band at 1784 cm^{-1} attributed to the symmet-

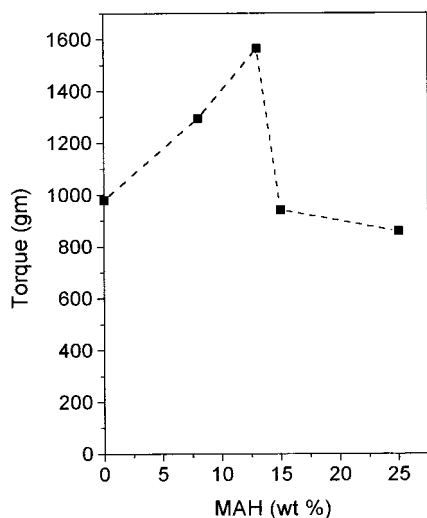


Figure 2 Torque after 400 s of processing as a function of MAH concentration. Processing conditions: 150°C, 55 rpm for 20 min, 0.2 wt % of benzoyl peroxide.

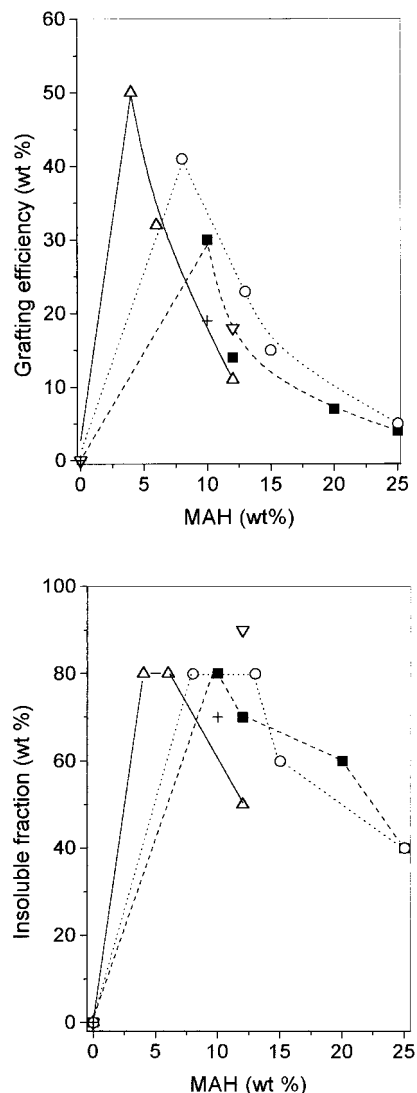


Figure 3 (a) Grafting efficiency, and (b) insoluble fraction of modified SBS as a function of initial MAH concentration. Reaction conditions: 0.1 wt % of benzoyl peroxide, 130°C (Δ); 0.2 wt % of benzoyl peroxide, 130°C (■); 0.3 wt % of benzoyl peroxide, 130°C (▽); 0.2 wt % of benzoyl peroxide, 150°C (○); and 0.2 wt % of benzoyl peroxide, 170°C (+).

ric C=O stretching. Five members cyclic anhydrides exhibit an intense absorption band near 1780 cm^{-1} and a weak absorption band near 1850 cm^{-1} due to symmetric and asymmetric C=O stretching, respectively.¹⁸ The asymmetric stretching of carbonyl, at 1850 cm^{-1} , could not be observed on SBS-g-MAH due to the low MAH-grafted concentration. No MAH homopolymer was isolated by extraction or detected by IR spectroscopy.

Electron donors such as *N,N*-dialkylamides and stearamide have been used as degradation

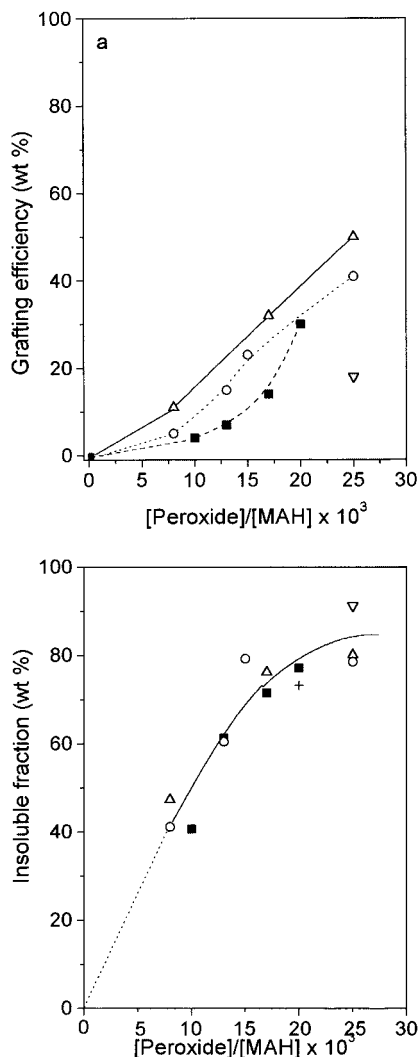


Figure 4 (a) Grafting efficiency, and (b) insoluble fraction as a function of [peroxide]/[AM]. Reactions conditions: 0.1 wt % of benzoyl peroxide, 130°C (Δ); 0.2 wt % of benzoyl peroxide, 130°C (\blacksquare); 0.3 wt % of benzoyl peroxide, 130°C (∇); 0.2 wt % of benzoyl peroxide, 150°C (\circ); and 0.2 wt % of benzoyl peroxide, 170°C ($+$).

control either in solution or in bulk modification of PP,²¹ LDPE,¹⁹ and EPR² with MAH.

The MAH grafting on SBS chains was also conducted in the presence of an aromatic diamine at the following reactions conditions: 12 wt % of MAH, 0.2 wt % of benzoyl peroxide, variable diamine concentrations, 150°C and 55 rpm in a mixer. Torque as a function of the reaction time was monitored (Fig. 6). The torque behavior of the reaction mixtures depends on the diamine concentration and on the time. The torque of the 12SBS₁ and the 12SBS₂ samples decrease after the addition of the MAH/BP/diamine mixture at

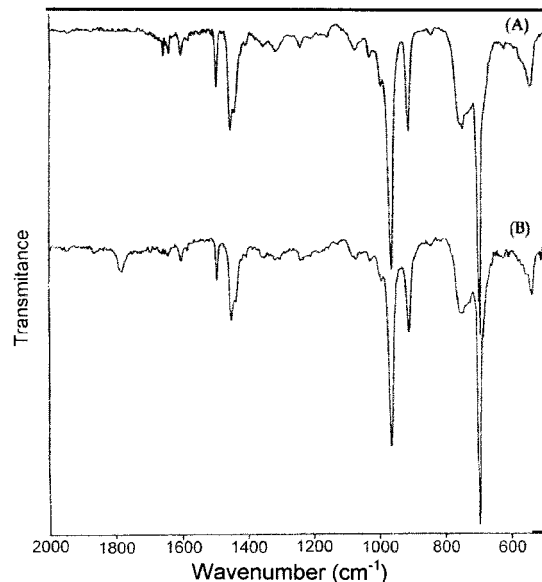


Figure 5 FTIR spectra: (A) SBS (B) purified SBS modified in the presence of 0.2 wt % of benzoyl peroxide and 13 wt % of MAH.

240 s and suddenly increases after the second addition of diamine, at 720 s mixture. Figure 7 shows the torque as a function of the molar ratio of diamine and anhydride at 480 s and 1140 s, after the first and the second addition of diamine, respectively (see Table III). The increase of torque

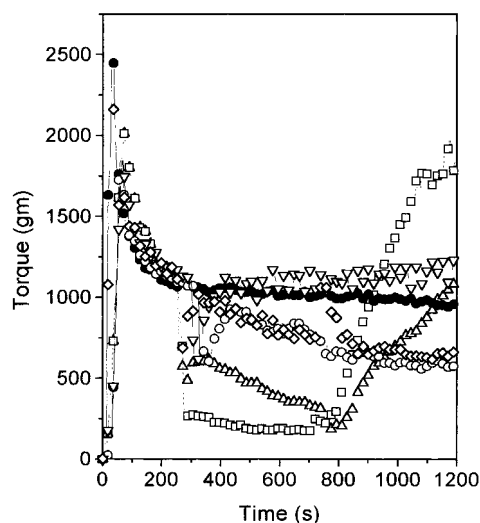


Figure 6 Torque as a function of the time for the reactions mixtures of SBS, 12 wt % of MAH, 0.2 wt % of benzoyl peroxide and different diamine concentration. Pure SBS (\bullet); 12SBS₁ (\square); 12SBS₂ (Δ); 12SBS₃ (\diamond); 12SBS₄ (\circ); 12SBS₅ (∇). Processing conditions: 150°C, 55 rpm for 20 min.

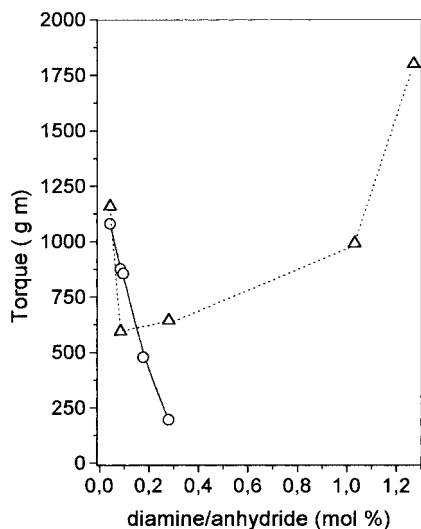


Figure 7 Torque as a function of the molar ratio of diamine and anhydride at 480 s (○) and 1140 s reaction (△), after the first and the second addition of diamine, respectively.

suggests an increase of molecular weight and crosslinking. It is also possible for a reaction between free anhydride and free diamine forming aromatic polyamide and polyimide. Solubility tests show that a fraction of the modified SBS, 12 SBS₁, and 12 SBS₂ is insoluble. On the other hand, 12SBS₃, 12SBS₄, and 12SBS₅ are soluble in ordinary solvents, suggesting the absence of an aromatic polyamide and polyimide. Diamine at a lower concentration is an efficient inhibitor to SBS crosslinking, which can occur through radical mechanisms. On the other hand, by higher concentration the diamine acts as a crosslinker in a reaction involving the nucleophilic attack of amine groups to carbonyl groups of the anhydride. The FTIR spectra sustain this last hypothesis.

The FTIR spectra of the SBS and the 12SBS₁ and 12SBS₂ after purification (extraction of free diamine and free anhydride with toluene) are shown in Figure 8.

The FTIR spectra of 12SBS₁ and 12SBS₂ samples show a new strong absorption band at 1712 cm⁻¹ due to the asymmetric carbonyl stretching, suggesting the conversion of the anhydride groups into carboxylic acid.¹⁸ The new absorption bands at 1518 and 1388 cm⁻¹ indicate the presence of primary amine groups and between 1600 and 1700 cm⁻¹ suggest the presence of amide and imide group. Therefore, the crosslinking of 12SBS₁ and 12SBS₂ probably occurs through

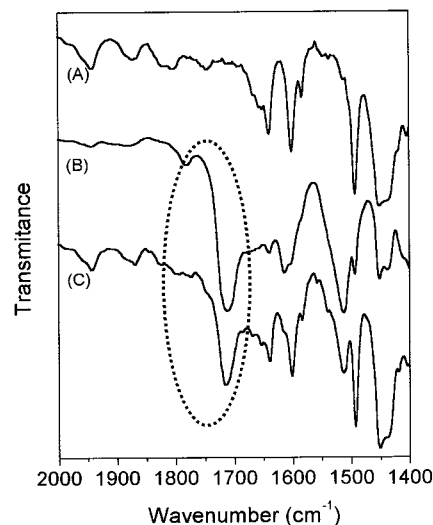


Figure 8 FTIR spectra of (A) SBS, (B) purified 12SBS₁ and (C) purified 12SBS₂.

amide and imide covalent bonds in a mechanism proposed in Figure 9. The intensity of the absorption at 1712 cm⁻¹ increases as the molar ratio of diamine and anhydride group increases, suggesting an improvement of the reaction extension leading to crosslinking of SBS and also to formation of polyamide and polyimide.

The anhydride content in the modified SBS determined by titration was 0.26, 0.33, and 0.20 wt % for 12SBS₃, 12SBS₄, and 12SBS₅, respectively. The anhydride concentration is low enough not to modify the mechanical and thermal properties of SBS but significantly improves its reactivity. SBS-*g*-MAH has been used to prepare reactive blends with functionalized PP.²²

CONCLUSIONS

It is possible to modify the SBS rubber with MAH in the melt using peroxide as an initiator. How-

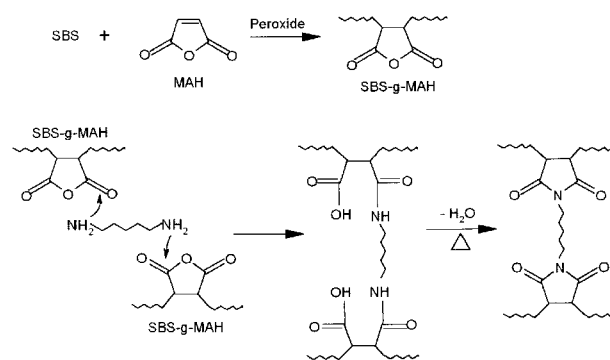


Figure 9 Schematic representation of the crosslinking of the modified SBS with diamine.

ever, the grafting efficiencies under the studied conditions are very low, and the grafting reaction is accompanied by undesirable crosslinking. The insoluble fraction is significantly minimized in the presence of a diamine.

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