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Functionalization of styrene-butadiene-styrene (SBS) triblock copolymer with maleic anhydride

Carlota H. F. Maurano, Liliane L. Portal, Ricardo Baumhardt Neto, Raquel S. Mauler ✉

Instituto de Química, UFRGS Av. Bento Gonçalves, 9500, 91510-970 Porto Alegre RS, Brazil
e-mail: Mauler@if.ufrgs.br, Fax: 55 51 3191499

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Summary

The thermoplastic elastomers have been widely used in polymer blends to improve their mechanical properties. This work is about the study of chemical modification of styrene-butadiene-styrene (SBS) with maleic anhydride (MA) by radical reaction. The functionalization reaction was carried out in a mixer Haake Rheomix 600 and the torque variation was monitored during the process. The products were characterized by Infrared Spectroscopy (FTIR) and crosslinking was evaluated by extraction. A calibration curve was plotted to determine the functionality. The results showed that it is possible to accomplish the functionalization reaction avoiding the crosslinking.

Introduction

The final properties of polymer blends are directly related to the quality of their morphology, which in turn depends on the rheological properties, on the composition, on the processing conditions and on the compatibility between the constituent of the blend [1]. The use of compatibilizing agents act in the interface reducing the interfacial tension, originating materials with characteristics of both constituent of the blend [2-4]. The increase in adhesion between the polymer phase may be related to the chain entanglements or through the covalent bonding of the polymer chains [5,6].

The compatibilizing agents are generally, block or graft copolymers that possess segments capable to interact with the components of the blend [3,4]. The graft or block copolymers can be obtained separately or during the blending (*in situ*) trough the reaction of the functional group introduced onto the polymer chain and the chain functional end group of the other component [1]. Several polymers have been functionalized with polar monomers for this purpose [7]. The efficiency of the compatibilizing agent depends on their molecular weight, the type of incorporated functional group and the concentration of these groups in the polymer chain [6].

The commercial importance of thermoplastic elastomers, as SBS and SEBS, has rapidly increased in recent years. These materials can be processed as thermoplastics and they present properties of rubber, as high resilience and elasticity. Thermoplastic rubbers are widely used in blends with polypropylene [8,9], Nylon [10] and polybutadiene [11]. SEB S-MA has been shown to be more efficient in reducing the interfacial tension of polyoliefins and polar polymers than EPR-MA, EVA-MA,

HDPE-MA and PP-MA[12]. Also, elastomer are one of the efficient asphalt modifier [13]. Effects of polymer content/structure and bitumen type on viscosity characteristics of SBS polymer modified bitumens have been investigated [14-16].
The functionalization of SBS with polar monomers will increase its compatibility with polar materials and has the advantage to be used without the hydrogenation process. In this study the fanctionalization reaction of MA onto SBS will be accomplished. The relationships between the MA and peroxide concentration will be established in order to obtain the incorporation of the monomer onto SBS chain, and to minimize the crosslinking reaction.

Experimental

Materials

The materials used in this study were SBS rubber (TR1061, Petroflex Ind. & Com.), Mw = 119000 g/mol, polydispersity = 1.35, styrene/butadiene = 20/80 mol. Butadiene 1,4/1,2 = 3/1 mol. Maleic anhydride (MA) was supplied by Produtos Quimicos Elekeiroz S.A and dicumil peroxide (DCP) by Aldrich Chemical Company Inc. The chemical products used in this work were of analytic grade and were used as received.

Functionalization reaction

The functionalization of SBS with MA was carried out in a Haake Rbeomix 600 mixer with fixed rotation speed of 40 rpm, during 10 min. The initiator concentration was in the range from 0.05 wt% to 0.1 wt% and MA concentration was varied from 2 wt% to 6 wt %. The products were purified by extraction in acetone during 4 h to remove the unreacted MA The products were dried and submitted to extraction with toluene in Soxhlet, during 48 h.

Characterization

The amount of MA incorporated onto polymer chain was measured by Infrared Spectroscopy (FTIR), in a BOMEM MB-102 apparatus, with zinc selenete crystal and incidence angle of 45°. The scanning interval of the analyze was from 4000 cm^{-1} to 620 cm^{-1}. The analyses were performed in films that were obtained in a Carver hydraulic press, Monarch Series, model 3710 ASTM. The products were submitted the pressure of 5 kN, during 2 mill, at 120°C.
The functionality determination was also made by hydrolysis followed by titration. The polymer was dissolved in THF and the solution was refluxed with water by 1 h. The solution was titrated with a KOH/EtOH 0.01 N solution and phenolphthalein as indicator.

Results and Discussion

A calibration curve was constructed using relative functionalization obtained from infrared spectroscopy and from the absolute functionalization obtained from the titration. The areas of the peaks at 1780 cm^{-1} and 1715 cm^{-1}, due to the carbonyl of the anhydride group and of the carboxyl acid group formed by the hydrolyze of the anhydride group, were used as internal standard. These areas were added and defined as A1. The area of the peak at 840 cm^{-1} due to C-H of the aromatic ring was defined as A2. The calibration curve was constructed plotting the A1/A2 versus the functionality obtained by titration. The functionality determination was accomplished through of the following calibration curve: F (wt%) = 0.04259 (A1/A2) + 0.0453, where F is functionality.

The functionalization reactions were performed in agreement with an experimental design of factorial type, that is a statistical method of multivariate analysis. In the factorial planning 2^k the factors are used in two levels and k corresponds to the number of analyzed factors [17]. The variables were anhydride and peroxide concentrations, each one in two level, forming a factorial 2^2 with 4 experiments. The reaction conditions were chosen after preliminary reactions. The studied responses were final torque, functionality, and conversion (ratio between the functionality and the MA concentration used). The factorial planning allows to determine the effect of each factor, as well as the interaction effect among the variables. The factor or interaction among factors effect is defined as the medium change on the response calculated when the factor level is altered of the smaller level for the largest [18].

The first set of reactions was accomplished at 160°C and the results are shown in the Table 1 (factorial A). The grafting sites are generated by various radicals attacking the polymer backbone [19-21]: primary radical abstracting an allyl hydrogen (1) followed by the incorporation of the MA (2). The SBS-MA radical will terminated abstracting an allyl hydrogen by chain transfer (3) [19-22]. The MA do not present tendency to homopolymerize [23].

$\mathrm{R{\bullet} + SBS \rightarrow SBS{\bullet} + RH}$ (1)
$\mathrm{SBS{\bullet} + MA \rightarrow SBS\text{-}MA{\bullet}}$ (2)
$\mathrm{SBS + SBS\text{-}MA{\bullet} \rightarrow SBS{\bullet} + SBS\text{-}MAH}$ (3)

Table1: Functionalization of SBS with MA at 160°C

MA (wt%)	DCP (wt%)	Torque (Nm)	F (wt%)	Conversion (%)
		Factorial A		
0	0	8	0	0
2	0.05	8	0.05	2.5
3	0.05	10	0.08	2.7
2	0.10	10	0	0
3	0.10	9	0.06	2.0
		Factorial B		
4	0.05	10	0.06	1.5
5	0.05	9	0.07	1.4
4	0.10	10	0.05	1.3
5	0.10	9	0.08	1.6

40 rpm, 10 min, conversion = (F wt% / MA wt%)*100

The crosslinking takes place trough the addition of SBS radical or SBS-MA radical to the double bond of SBS block copolymer mainly to the vinyl double bond [24]. Also the crosslinking will be formed by polymer radical combination [19]. The polystyrene segments of the block copolymer are phase separated and are not expected to participate of the process [25]. The benzyl hydrogen is more labile then the allyl butadiene hydrogen and if it is abstracted a less reactive radical is formed due to its high stability [19].

The variables effects on functionality, torque and conversion are shown in the Figure 1. In the factorial A, the MA concentration presented positive effect on the functionality, conversion, and final torque. The positive effect on torque did not mean that crosslinking took place, because the products remained soluble after 48 h of extraction (with toluene) in Soxhlet. The increase in DCP concentration decreased the functionality and conversion response but the interaction between MA and DCP was positive for both.

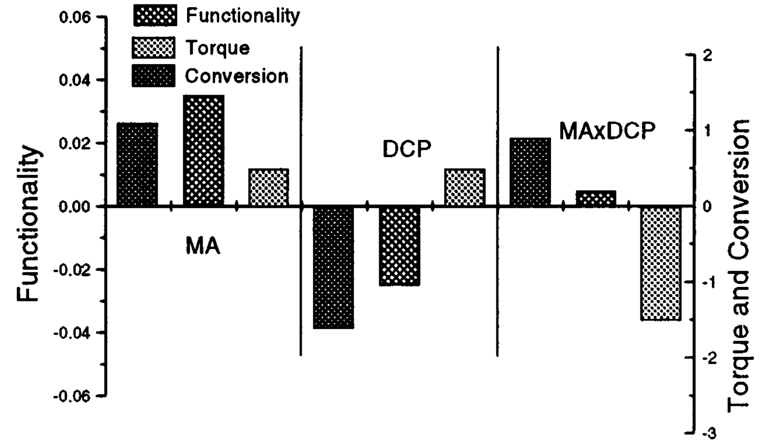

Figure 1: Effects estimated on final torque, functionality and conversion - Factorial A

According to the positive effect of the MA concentration, a new factorial was accomplished (factorial B), where the monomer concentration was increased and the other variables were maintained as before. The results of factorial B are shown in the Table 1 and the effects of the factors are shown in the Figure 2.

In this new factorial the MA concentration presented positive effect on the functionality and conversion, but the increase in MA concentration did not lead to an increase in functionality in relation to the factorial A. In this temperature (160°C) the concentration of formed radicals, by initiator decomposition, was not enough to promote the satisfactory anhydride incorporation onto the polymer due to the high half-life of the peroxide.

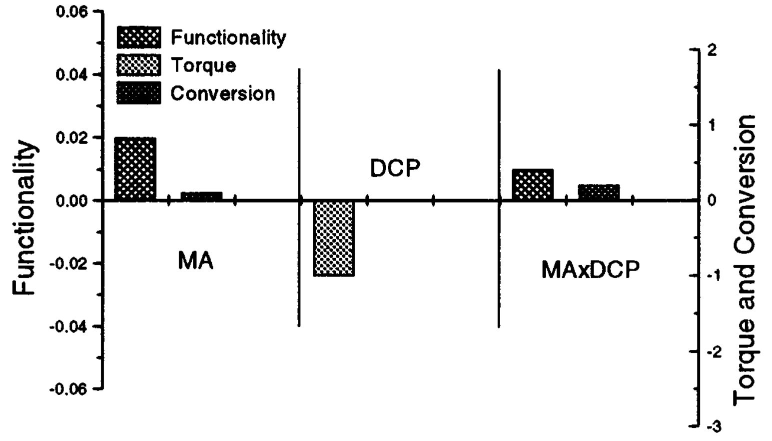

Figure 2: Effects estimated on final torque, functionality and conversion - Factorial B

New experiments were accomplished at 170°C. Two new factorial (factorial C and D) were developed with the MA and DCP concentrations maintained as before. The factorial C and D results are in the Table 2. The effects of the factors were also calculated and they are shown in the Figure 3 (factorial C) and Figure 4 (factorial D).

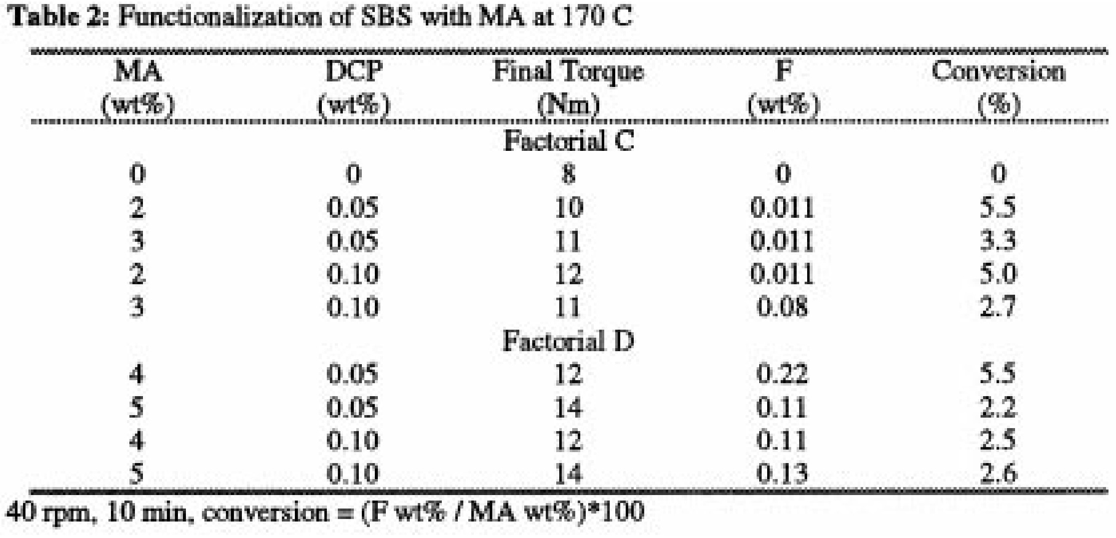

Table 2: Functionalization of SBS with MA at 170 C

MA (wt%)	DCP (wt%)	Final Torque (Nm)	F (wt%)	Conversion (%)
		Factorial C		
0	0	8	0	0
2	0.05	10	0.011	5.5
3	0.05	11	0.011	3.3
2	0.10	12	0.011	5.0
3	0.10	11	0.08	2.7
		Factorial D		
4	0.05	12	0.22	5.5
5	0.05	14	0.11	2.2
4	0.10	12	0.11	2.5
5	0.10	14	0.13	2.6

40 rpm, 10 min, conversion = (F wt% / MA wt%)*100

When the reactions were realized at 170°C, the functionality increased compared to the factorials A and B. At 170°C the dicumyl peroxide half-life is short favoring the formation of radicals. However the MA and DCP concentrations presented a negative effect on the conversion and a small effect on the functionality (Figure 3). These reactions also presented a small increase of the torque in relation to factorial A and B, however the products were still soluble.

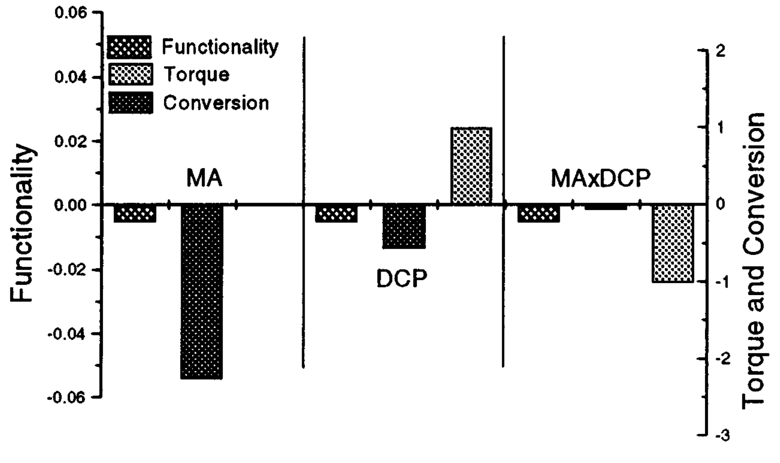

Figure 3: Effects estimated on final torque, functionality and conversion - Factorial C

As the MA concentration did not present effect on the torque (Figure 3) and since its effect was small in the functionality, other reaction set (factorial D) was accomplished, where the MA concentration was increased. Figure 4 showed that the concentration of MA presented positive effect in the torque but the DCP concentration did not present effect. The MA and DCP concentrations presented negative effect on functionality and conversion. However the interaction between MA and DCP presented positive effect.

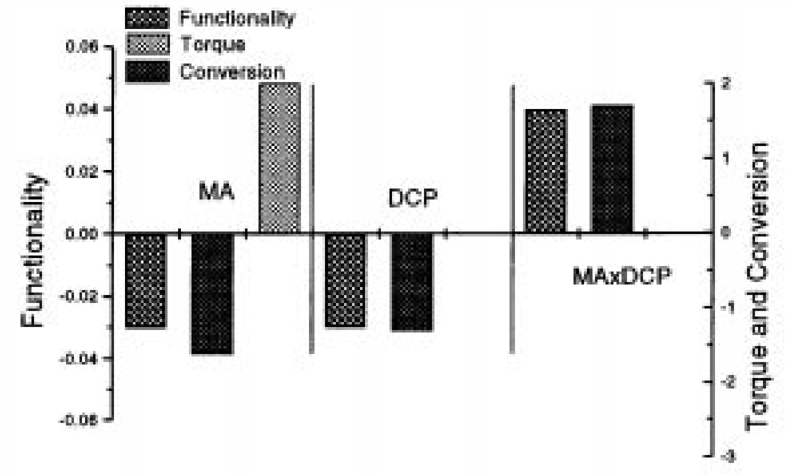

Figure 4: Effects estimated on final torque, functionality and conversion - Factorial D

According to these results complementary reactions were accomplished to evaluate the best reaction conditions. In these set of reactions it was used an intermediate concentration of DCP (0.075 wt%) since the increase of DCP level presented a negative effect on functionality and conversion. The MA concentration presented negative effect on functionality but its interaction effect with DCP was positive. Then the MA level was used as before and with one higher level (6.0 wt%). The results of these complementary reactions are shown in the Table 5. When the functionalization reaction was accomplished without DCP but in the presence of 3 wt% of MA, it was possible to incorporate 0.11 wt% of MA with a very low increase in torque. This incorporation was due to the formed radicals during the shear process. The MA incorporation in DCP absence is not suppose to occur through ene reactions. Since it was shown that very severe conditions were needed to favor this reaction, as very low molecular mass, very high MA concentration, high temperature and pressure and long reaction time [26,27]. The presence of DCP alone on the process was not enough to provoke a high increase on the torque.

Table 5: Functionalization of SBS with MA at 170 C - Complementary reactions

MA (wt%)	DCP (wt%)	Final Torque (Nm)	F (wt%)	Conversion (%)
0	0.1	10	0	0
3	0	9	0.07	2.3
4	0.075	15	0.04	0.9
5	0.075	14	0.11	2.2
6	0.050	12	0.06	1.0
6	0.075	13	0.20	2.8

40 rpm, 10 min, conversion = (F wt% / MA wt%)100

All the results of the factorial designs at 170°C and complementary reactions were plotted as a surface plot to best visualize the tendency of these results.

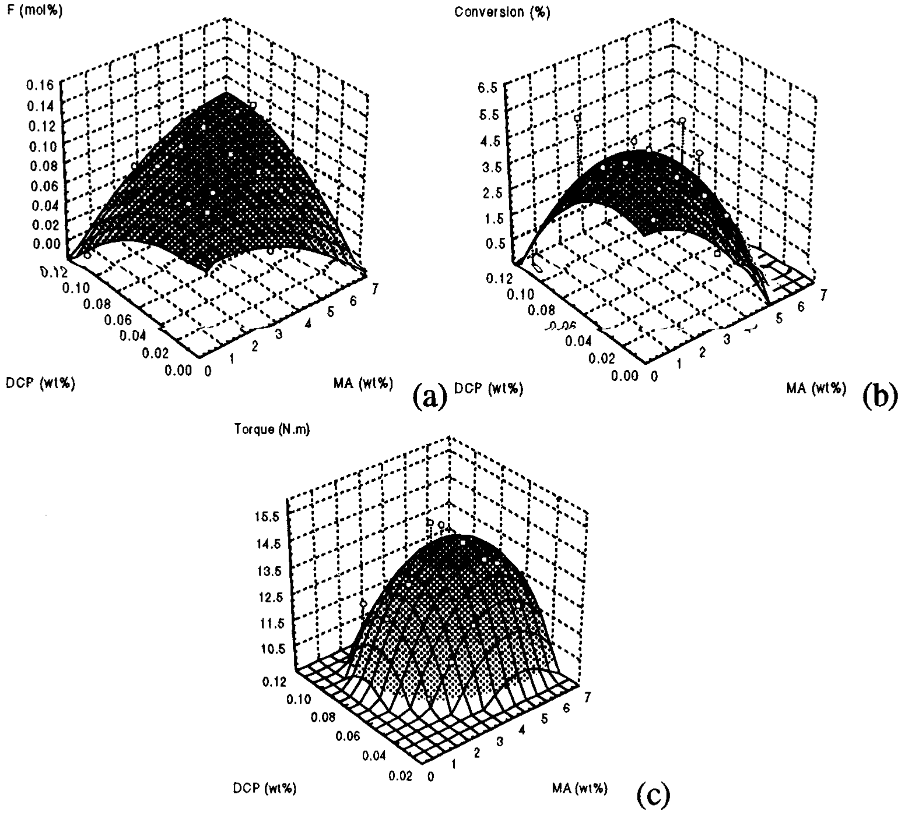

Figure 5: Effect of MA and DCP concentrations on (a) functionality (b) conversion (c) torque

Figure 5a suggests an ideal ratio between MA and DCP to reach highest functionality levels. The functionality increases with the simultaneous increase of MA and DCP concentrations. Although the functionality increase with MA concentration this increase was very low to mean an increase on conversion, since the conversion is the ratio between the functionality and the MA concentration used. The surface graph (Figure 5b) shows the changes in conversion with MA and DCP concentrations, and the maximum conversion is reached at low level of MA and low to intermediate level of DCP. The Figure 5c displays the results of the torque and they reached a maximum region at 4 wt% of MA and 0.08 wt% of DCP.

CONCLUSION

The results of functionalization reaction showed that there was a good relationship among the functionality obtained by titration and the analysis of infrared spectroscopy, making possible the construction of a calibration curve.

The functionalization reaction of SBS with MA could be accomplished without crosslinking reaction. The largest functionality values were obtained at 170°C due to the higher decomposition rate of the peroxide at this temperature. The increase of the torque is related to chain extension that is favored by the presence of macroradical that did not react with MA. In these conditions the torque presents a maximum value when MA and DCP concentration tended to intermediate to high level. The functionality increased with the increase of ratio between DCP and MA concentration.

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