

Preparation of Hydroxyl-Functionalized SEBS for *In Situ* Graft Reaction Compatibilizing Agents

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Received 7 August 1996; accepted 5 December 1996

ABSTRACT: An hydroxyl-functionalized SEBS was obtained when maleated SEBS was reacted with a low molecular weight compound, 3-amine-1-propanol (AMP), in toluene solution. The higher nucleophilicity of the primary amine in the AMP favored the imide formation with negligible self-crosslinking in the SEBS. The SMA was used to probe the graft compatibilization reaction with the hydroxyl-functionalized SEBS. Analogue monomer reactions were made to investigate the mechanisms of the reaction products in the monomer-polymer and polymer-polymer reactions. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2519–2528, 1997

Key words: coupling agent; SEBS; compatibilizer; amine/hydroxyl bifunctional monomer; coupling reactions

INTRODUCTION

Compatibilization of polymer blends has been improved by various techniques including reactive compatibilization.¹ In this method, reactive polymers are used to produce *in situ* graft copolymers with segments miscible with each component of the blend.² Reactive polymers containing anhydride, carboxylic acid, amine, hydroxyl, and epoxide groups are among the most studied compatibilizing agents in the literature.^{1–3} The highly reactive maleic anhydride (MA) is a very common monomer used to obtain functionalized polymers like polyethylene-MA, polypropylene-MA, and poly(styrene-co-MA) (SMA). These materials have been widely used in reactive compatibilization studies.⁴ Different methods of preparation of these and other reactive polymers have been described elsewhere.⁵ In most studies of the use of

maleated compatibilizing agents the highly electrophilic MA moiety is observed to undergo rapid reactions with stronger nucleophiles such as the primary amine end groups of nylon.⁶

Reactive compatibilizers can be also produced by means of a third component (coupling agent) when the two polymers do not react independently. In this strategy, a low molecular weight bifunctional coupling agent undergoes separate reactions with each of the two immiscible polymers to form the *in situ* graft copolymer.

Several bifunctional monomers have been reported to be useful as coupling agents. Polyethylene containing carboxylic acid groups has been coupled with polystyrene containing anhydride groups using different types of diamines through reactive melt processing.^{4,7}

Another coupling agent, dimethylaminoethanol, has been used to compatibilize SMA/bromo butyl rubber blends reducing the size of the dispersed phase by fivefold.⁸ Other types of monomers such as peroxides⁹ and organosilanes¹⁰ have been also used as coupling agents.

In the present work, we will explore the use of

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Contract grant sponsor: Mexican National Council of Science and Technology (CONACyT).

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a low molecular weight coupling agent as a pathway to hydroxyl-functionalized polymers, which in turn, can participate in graft compatibilization reactions. Specifically, 3-amine-1-propanol (AMP) will be employed in a reaction with maleated SEBS rubber. Here, the selective reaction of the highly nucleophilic primary amine group will be used to generate predominantly hydroxyl-functionalized SEBS rubber materials. In a second step, the hydroxyl-functionalized SEBS will be used to react with an SMA copolymer. The SMA copolymer simply represents a highly reactive backbone structure that is convenient for this study. The hydroxyl-functionalized SEBS materials could also be useful in compatibilization reactions with materials such as acyl functionalized polycarbonate or polyesters. In this work, the reaction products and relative rate of reaction of the amine and hydroxyl moieties are first investigated using analogous reactions of the monomer species. Following this, blends of SMA, and modified SEBS-*g*-MA are observed. The monomer and polymer reaction products are studied by means of FT-IR and NMR. Here, we limit the scope of the reactions to those conducted in solution to clearly analyze the reaction mechanism.

Background: Proposed Reaction Schemes

The generalized reaction of an amine hydroxyl-functionalized coupling agent with a maleated polymer is shown in Figure 1. The reactions between maleic anhydride and amine and hydroxyl groups have been widely studied.³ The kinetics of the imidization reaction of the anhydride moiety has been investigated in solution with the opening and the cyclization of the amide acid.¹¹ For this work, the reaction of the maleated SEBS materials could proceed by two pathways, with the first step being the conversion of maleic anhydride by an unreacted bifunctional AMP molecule. The relative reactivity of the amine and hydroxyl groups will determine the population of desirable hydroxyl and amine-functionalized materials that remain at this first reaction stage [Fig. 1(b)]. Naturally, the reaction could proceed when the resultant hydroxyl or amine-functionalized materials encounter an unreacted maleic anhydride moiety. The consumption of maleic anhydride in this way leads to crosslinking and an undesirable reaction product.

The relative nucleophilicities of the two functional moieties favors the amine-MA reaction as opposed to that of the hydroxyl-MA reaction.

However, it is not understood to what extent the relative reactivities of the two groups will affect the ultimate distribution of hydroxyl-functionalized SEBS materials. To examine the magnitude of the relative rates of reaction for the amine and hydroxyl groups, the work will first investigate the reaction products of the analogous monomer-monomer reactions.

EXPERIMENTAL

Materials

The polymers used in this work were a SEBS-*g*-MA containing 29 wt % of styrene and 2 wt % of MA grafted on the rubber segment, $M_w = 66687$, $M_n = 46043$ $M_w/M_n = 1.44$ (Kraton F1901x from Shell Chemical Co.) and a SMA random copolymer containing 8 wt % of MA, $M_w = 178,283$, $M_n = 90,101$, $M_w/M_n = 1.97$ (Dylark 232 from Arco Chemical). Propanol, propylamine, succinic anhydride, and AMP (3-amino-1-propanol) were used without further purification. Toluene, hexane, and dichloromethane were dried and distilled before use. With the exception of the polymeric materials, all chemicals were obtained from Aldrich Chemical Co. (Milwaukee, WI).

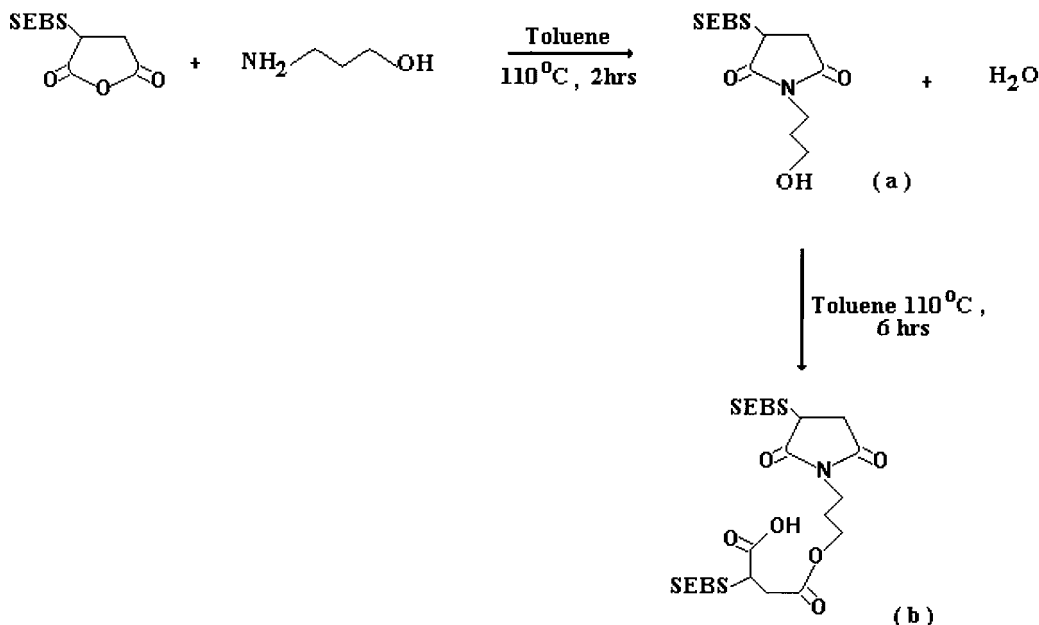
Analysis

The FT-IR spectra were obtained by means of a Nicolet 550 spectrometer with 0.5 cm^{-1} resolution. Polymer films for FT-IR analysis were prepared by solution casting from a 5 wt % solution in anhydrous dichloromethane. The films were dried in a vacuum oven at 80°C for 1 night and stored in a desiccator prior to use. Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian Gemini-200 MHz using deuterated chloroform at 25°C.

Coupling Agent Reactions

Tables I and II show a summary of the polymeric and monomeric reactions, respectively, listing the wt % of the copolymers, and the molar ratio between functional groups for each reaction. The experimental conditions of the reactions are described individually below including (a) monomer analogue coupling reactions and (b) polymer-coupling reactions.

Step 1)



Step 2)

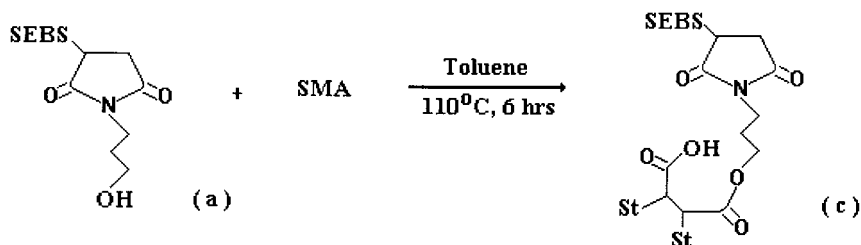


Figure 1 Reaction scheme 1. Two-step reaction showing the selective reaction of the AMP coupling with SEBS and then with SMA.

Monomer Analogue Coupling Reactions

Reactions of Succinic Anhydride with Functional Monomers. 2.5 g (0.025 mol) of succinic anhydride was dissolved in 50 mL of dry toluene contained in a 100 mL glass flask coupled with condenser and stirrer. The solution was heated at 50–60°C until complete dissolution and then cooled to about 30°C. Then, 0.025 mol of the corresponding monomer (1.87 g of AMP, 1.5 g of propanol or 1.47 g of propylamine) was added slowly while stirring. The mixtures were refluxed for 8 h, taking aliquots at 0.25, 1.0, 2.0, 4.0, 6.0, and

8.0 h to follow the progress of the reaction by FT-IR. With the equimolar reaction of succinic anhydride with propylamine, white crystals were obtained which exhibited a melting point between 89–90°C. The material was readily soluble in solvents such as THF and acetone, and insoluble in hexene, benzene, and toluene. This powder was recrystallized from methylene chloride : hexane (1 : 3 by vol) and identified by FT-IR and $^1\text{H-NMR}$. For the AMP reaction, a transparent colorless oil was obtained. This product was washed with cool toluene and dried in a vacuum oven. Finally, with the propanol reaction, the expected

Table I Molar Ratios of Functional Groups in Polymeric Reactions

Reaction	SMA wt %	SEBS- <i>g</i> -MA wt %	Coupling Agent	Molar Ratio NH ₂ : MA	Molar Ratio OH : MA
Two Step	80	20	AMP	1 : 11.5	
One Step	80	20	AMP	1 : 2.6	
SEBS- <i>g</i> -MA and PA		100	PA	1 : 1	
SEBS- <i>g</i> -MA and propanol		100	Propanol		1 : 1 20 : 1

product was detected by FT-IR, but it could not be isolated. The equimolar mixture of succinic anhydride and AMP refluxed in toluene for 6 h produced a viscous, colorless, and transparent oil. This compound is not soluble in almost all polar and nonpolar common solvents with the exception of dimethylsulfoxide and water.

Polymer-Coupling Reactions

*Two-Step Reaction of SMA/SEBS-*g*-MA with AMP.* In a first step, 3 g of SEBS-*g*-MA (6×10^{-4} mol of MA) were dissolved in 150 mL of dry toluene in a 500 mL glass flask coupled with condenser and stirrer. Then, 0.0444 g (6×10^{-4} mol) of AMP dissolved in 20 mL of toluene were added to the flask and the mixture was refluxed for 8 h. To follow the progress of the reaction, aliquots of 25 mL were taken at 0.25, 1, 2, 4, and 6 h and analyzed by FT-IR. Additionally, the insoluble fractions of the solutions were determined by an adapted method (ASTM-3616). Finally, the solvent from aliquots was evaporated and the obtained film was dried at 80°C for 12 h in a vacuum oven.

In the second step of the reaction, 2 g of the functionalized polymer (SEBS-*g*-MA/AMP) were dissolved in 100 mL of toluene. Then, 200 mL of a 4 wt % SMA toluene solution was added and the mixture was refluxed for 6 h at 110°C. Thin films were then obtained by evaporating the sol-

vent and drying for 12 h at 80°C in a vacuum oven.

To investigate the extent of crosslinking, the SMA/SEBS blends were also combined with the AMP in a one step reaction (Fig. 2). To carry out this reaction, 2 g of SEBS-*g*-MA (4×10^{-4} mol of MA) were dissolved in 150 mL of dry toluene in a 500 mL glass flask coupled with condenser and stirrer. Further, 8 g of SMA (6.5×10^{-3} mol of MA) were dissolved in 150 mL of toluene and added to the flask. Then, 20 mL of a solution of AMP (MA : AMP 2.6 : 1) in toluene were added to the solution. The mixture was refluxed for 8 h and aliquots of 25 mL were taken at 0.25, 1, 2, 4, and 6 h to follow the progress of the reaction as noted above. Thin films were prepared using the same method as that in the previous section.

RESULTS AND DISCUSSION

Anhydride Analogue Reactions

The reaction products of the proposed coupling schemes were first explored via the use of the mono- and bifunctional coupling analogues with succinic anhydride. The NMR and FT-IR analysis of the succinic anhydride reactions with propylamine, propanol, and aminopropanol follows accordingly.

The reaction of propylamine with succinic anhydride showed evidence of both amide acid and imide formation, depending of the nature of the reaction conditions. The ¹H-NMR spectrum of the uncatalyzed reaction product is shown in Figure 3(a). The ring-opening reaction mechanism of the succinic anhydride is clearly evident from the acidic hydrogen formation of the COOH group at 9.9 ppm. This is supported by the following signals in the FT-IR spectrum [Fig. 3(b)]: N-H group at 3315 cm⁻¹, COOH group at 1719 cm⁻¹, and carbonyl signal of the amide group at 1642

Table II Molar Ratios with Different Monomers in Succinic Anhydride (SA) Reactions

Monomer	Molar Ratio SA : Monomer
AMP	1 : 1
PA	1 : 1
Propanol	1 : 20

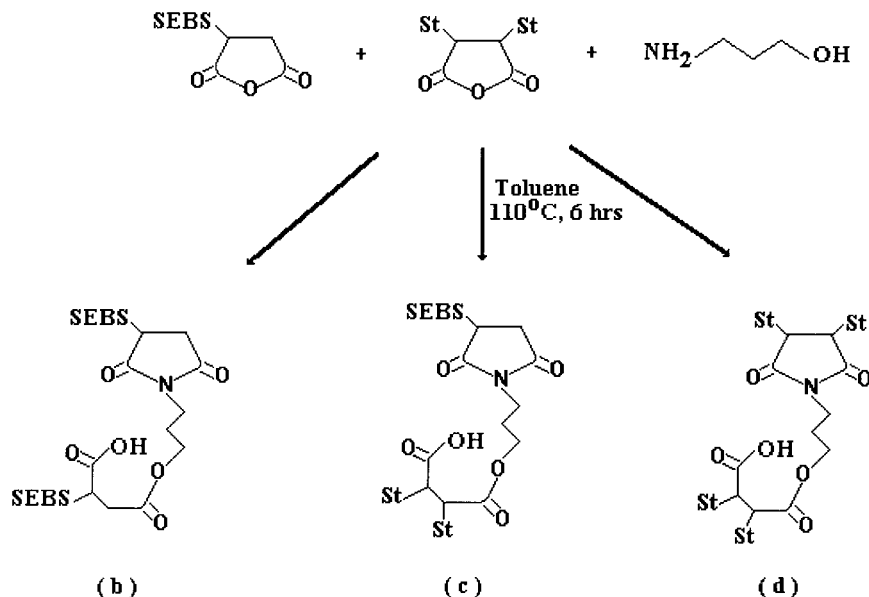


Figure 2 Reaction scheme 2. One-step reaction where coupling agent and polymers are combined simultaneously.

and 1584 cm^{-1} . When a small amount (1 mol %) of sulfuric acid catalyst is used in combination with water removal, the reaction products contain a substantially higher concentration of imide. The $^1\text{H-NMR}$ spectrum shows signals from both cyclic and acyclic compounds. The FT-IR spectrum shows a strong signal at 1730 cm^{-1} corresponding to the carbonyl group of the imide, and signals at 1631 and 1540 cm^{-1} corresponding to the amide group. The imide formation is observed only when a catalyst (H_2SO_4) is added to the reaction and water is removed, at longer reaction times (6–8 h) the relationship between amide acid and imide is 1 : 3.

With the analogue reaction of succinic anhydride with propanol, the hydroxyl functional group is by far less reactive than that observed in the reaction with propylamine. In the equimolar reaction of succinic anhydride and propanol, the esterification product was not observed by FT-IR. To produce the esterification product, a 20 : 1 propanol : succinic anhydride mol ratio reaction was conducted for 8 h at the same temperature. With these extreme stoichiometric conditions, the esterification product was observed; however, a significant amount of succinic anhydride remains still unaffected, indicating the lower nucleophilicity of the alcohol group, compared with the amine group. Other kinds of catalysts, like pyridine, with higher activity than acids and Lewis acids could

be used in anhydride-alcohol reactions,¹² increasing the esterification product formation.

In accord with the relative reactivity of the monofunctional analogues, the anhydride reaction with aminopropanol indicates preferential amine reaction, leaving the hydroxyl functionality in the reaction product. The $^1\text{H-NMR}$ spectrum of the AMP reaction product is shown in Figure 4(a). The notable displacements include $\delta = 1.5$ ppm, (t, 2H, CH_2OH), 2.35 ppm, (dt, 2H, $-\text{CH}_2-$), 3.15 ppm (2H, m, $\text{CH}=\text{CH}$), 3.45, (2H, $\text{NH}-\text{CH}_2$, t), 6.25, (1H, $\text{N}-\text{H}$), 7.8–8.0 ppm, (s, 1H, COOH). In agreement with the NMR results, the FT-IR spectrum of this compound [Fig. 4(b)] shows a wide and strong signal of the alcohol group at 3350 cm^{-1} . In addition to the hydroxyl stretch, a wide and medium intensity signal is shown at 1715 cm^{-1} , corresponding to the carbonyl group of carboxylic acid with amide signals at 1650 and 1571 cm^{-1} . Again, when catalytic amounts of sulfuric acid are added, the imide group becomes more dominant.

According to the above results, the AMP material, which contains both amine and hydroxyl functionality, could be a selective monomer for the compatibilization of polymer pairs, which both contain maleic anhydride functionality. After demonstrating the equivalent reaction selectivity in maleated polystyrene materials, a reactive coupling scheme is demonstrated involving SMA and maleated SEBS rubber.

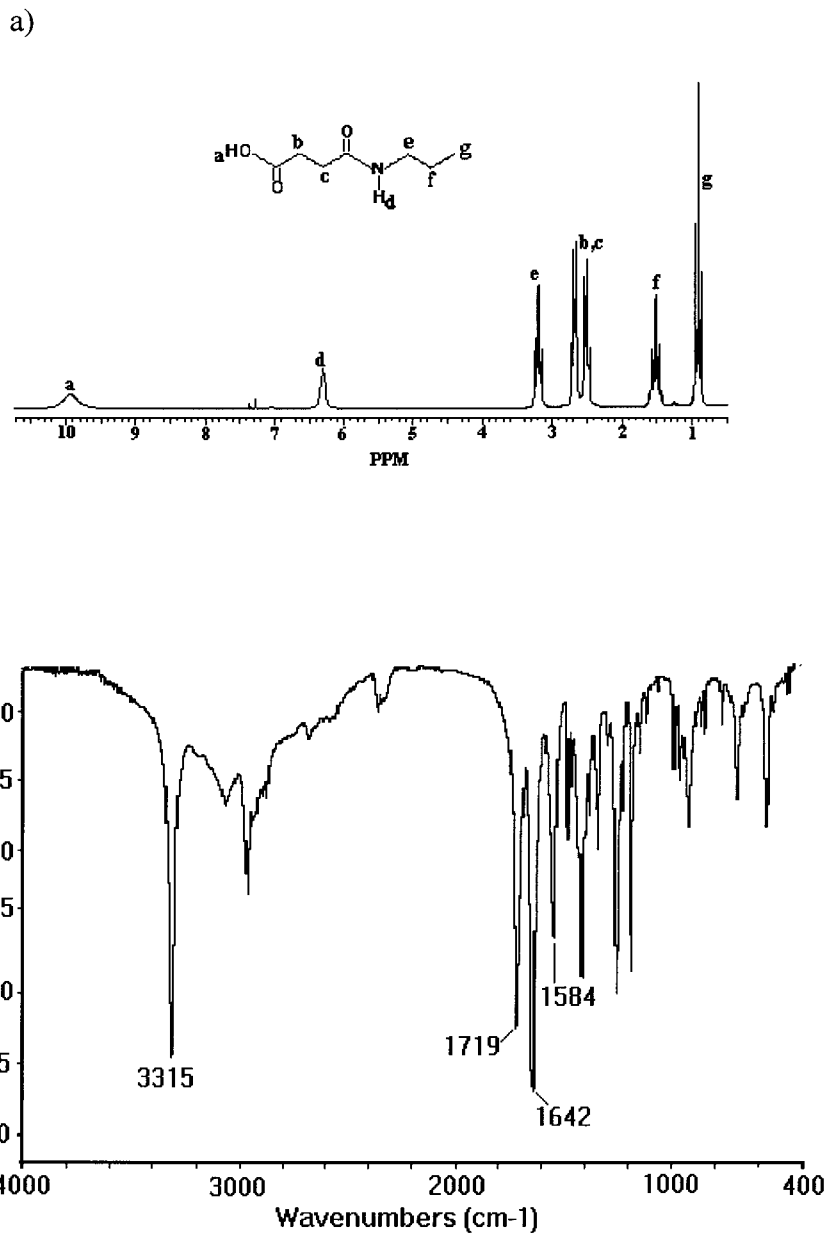


Figure 3 NMR (a) and FT-IR (b) spectra of the reaction product between succinic anhydride and propylamine (PA).

Polymer Analogue Coupling Reactions

To confirm the identification of the reaction products and the reaction selectivity of the AMP coupling agent, the reactions of the monofunctional amine and hydroxyl analogues were examined with respect to time of the reaction of maleated SEBS rubber systems. The reaction progress of the individual reactions of the propylamine and propanol with SEBS-*g*-MA are depicted in Figure 5. The diminution of the peak height of the maleic

anhydride signal at 1780 cm^{-1} related to the 1942 cm^{-1} peak, is plotted as a function of time of reaction in Figure 6. Under identical reaction conditions, the amine-anhydride reaction on the polymer backbone is predominant. The maleic anhydride-alcohol reaction shows virtually no progress after 6 h of reaction time.

More complete analysis of the FT-IR spectra of the SEBS-MA reaction with propylamine clearly indicates imide formation without the presence of acid catalyst. The amide (1650 and 1543 cm^{-1})

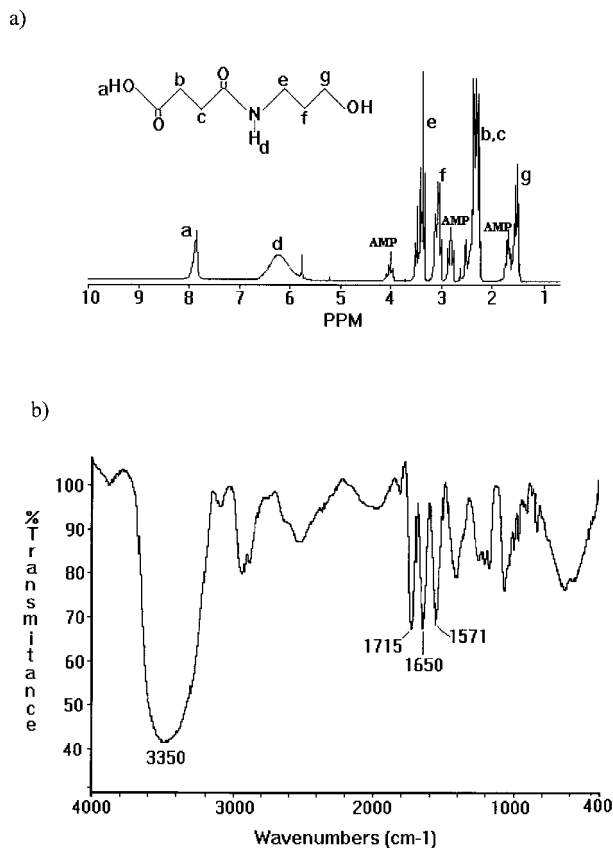


Figure 4 NMR (a) and FT-IR (b) spectra of the reaction product between succinic anhydride and aminopropanol (AMP).

and the carboxylic acid (1711.1 cm^{-1}) groups appear during the first hour of reaction [Fig. 5(a)]. At 4 h, the imide is clearly evident (1730 cm^{-1}) and at 6 h of reaction, no other changes were observed. Taking into account the low reactivity of the alcohol group, the SEBS-*g*-MA was reacted with a large excess of propanol (1 : 20 relationship). In this case, the ester group (1738 cm^{-1} signal), was not observed until 4 h of reaction. At 8 h, a considerable amount of MA remains unreacted [Fig. 5(b)]. Interestingly, we observed a considerable difference between the rate formation of amide in SEBS-*g*-MA and SMA reacted separately with propylamine. As a rule, we expected a higher reactivity in SMA than in SEBS-*g*-MA because of its higher MA concentration, but we observe just the opposite. This fact could be explained according to the availability to react for the MA in both copolymers. In SMA, the higher size of the aromatic rings could cause some hindrance around the MA, compared with the grafted form contained in the SEBS-*g*-MA, where MA is

hanging from a simple backbone chain (ethylene-buthylene part).

Polymer-Polymer Coupling Reactions

The monomeric coupling agent (AMP), used in the compatibilization reaction of the maleated SEBS and SMA, showed, as was expected, selective reactivity. First, hydroxyl-functionalized SEBS was formed in a reaction with AMP and then compatibilization reactions were carried out with SMA in a second step. In addition to following the progress of the reactions by FT-IR, the amount of insolubles was also tracked to determine the levels of coupling reactions. It is important to understand that insolubles, per se, are not a reflection of favorable coupling reactions

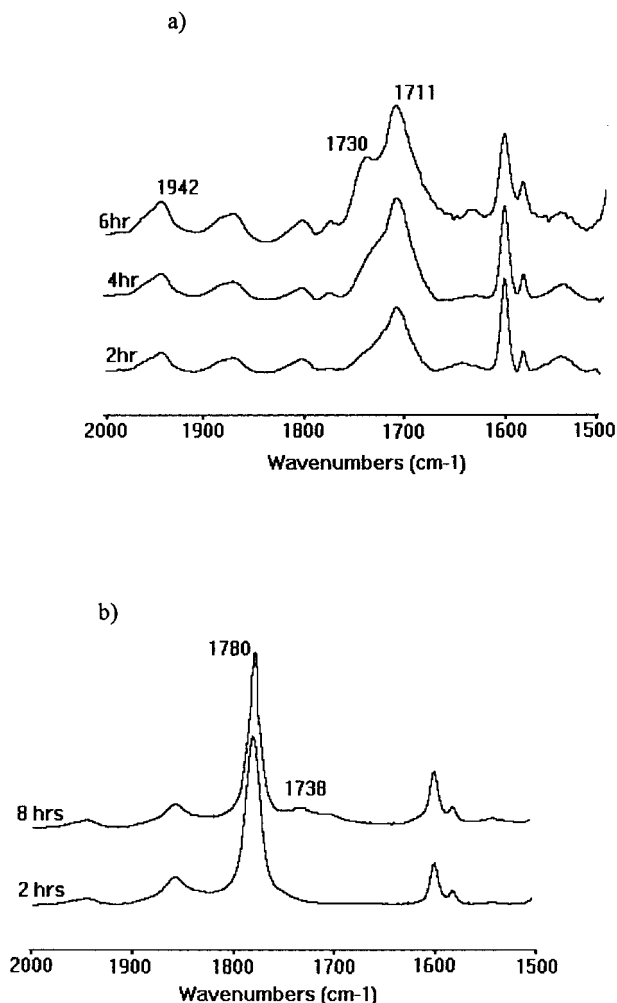


Figure 5 FT-IR spectra reaction of SEBS-*g*-MA with propylamine (a) and propanol (b) at various reaction times.

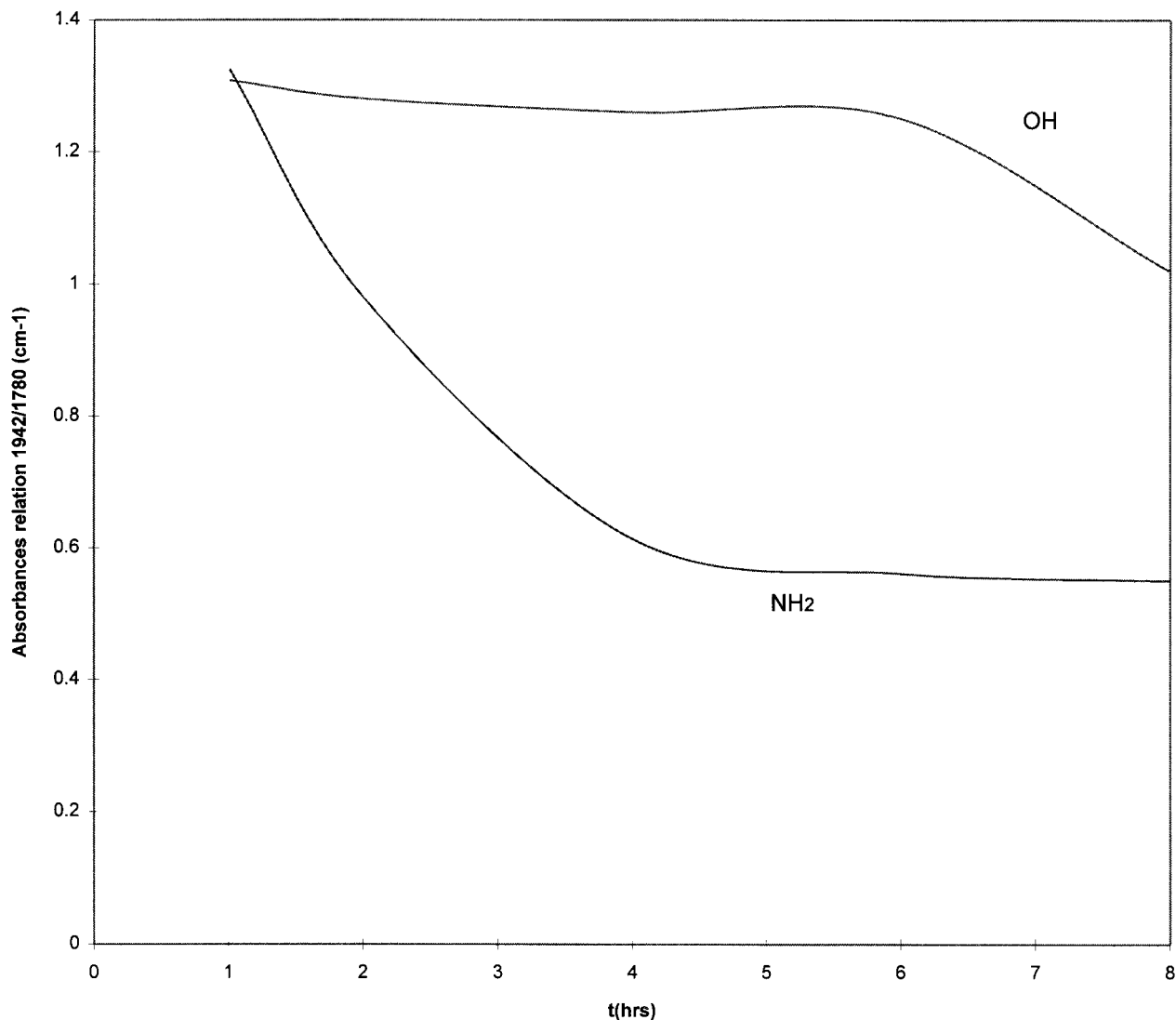


Figure 6 Consumption of maleic anhydride (MA) in SEBS-*g*-MA during equimolar reactions with propylamine (NH₂) and propoanal (OH). The reaction is depicted by the diminution of the relative FT-IR peak intensity of MA at 1780 cm⁻¹.

between two different maleated species, but also represents unfavorable crosslinking reactions.

In a first step, the maleated SEBS was reacted with the AMP with very low levels of self-crosslinking being observed. By means of the insoluble wt % determination, the crosslinking increases with the reaction time, which agrees well with the FT-IR observations. The insoluble fraction at 2, 4, 6, and 8 h was 0, 0.43, 2.3, and 5.4 wt %, respectively. For subsequent reaction with SMA, the 4-h reaction product with minimal self-crosslinking was selected.

The FT-IR spectra of the SEBS-*g*-MA/AMP reaction products (Figs. 7 and 8) show that the

MA groups react rapidly with AMP. It is assumed that the reaction readily occurs as it is represented in the reaction scheme 1 (Fig. 1).³ Initially, the amine group reacts with the MA forming the amide and carboxylic acid functions (cycle rupture), and then both functions react with each other forming a cyclic imide group through a condensation mechanism. FT-IR spectra of aliquots taken every 2 h show evidence of such reaction. The FT-IR spectrum of the reacted SEBS-*g*-MA with AMP (refluxed for 2 h) is shown in Figure 7. The ring opening of the MA of the SEBS-*g*-MA is confirmed by the presence of the amide signals at 1647 and 1545 cm⁻¹ characteristics of the car-

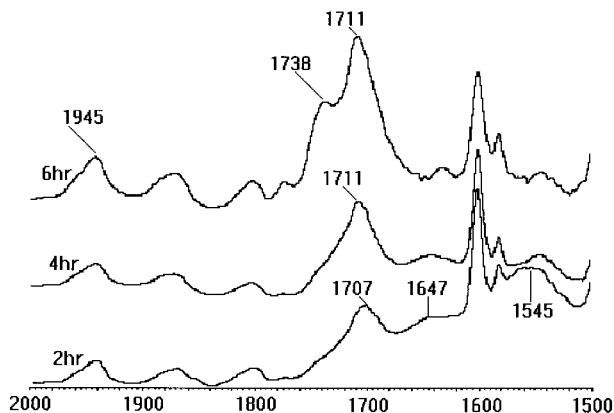


Figure 7 FT-IR spectra of the SEBS-*g*-MA and AMP at 110°C in solution showing imide formation (1711 cm^{-1}) with respect to time.

bonyl group of the amide and by the carbonyl group of the carboxylic acid function at 1707 cm^{-1} . Figure 7 shows the FT-IR spectrum of reacted SEBS-*g*-MA with AMP, refluxed during 4 h. The wide and medium intensity signal at 1711 cm^{-1} corresponds to the carbonyl group of the imide function, which was formed by cyclization. The FT-IR spectrum of the aliquote taken at 6 h is also shown in Figure 7. Here, a new signal (shoulder) appears at 1738 cm^{-1} corresponding to the ester group arising from the reaction between the free alcohol group of the maleimide and the anhydride group of the SEBS-*g*-MA. The FTIR spectrum at 8 h is similar to that obtained at 6 h.

In a second stage, the 4-h product was reacted with SMA to affect compatibilization. This later reaction occurs as it is represented in step 2 of

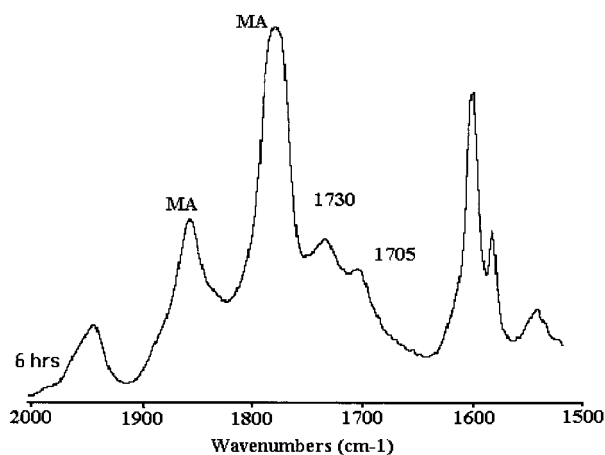


Figure 8 FT-IR spectrum of the compatibilization reaction between hydroxyl-functionalized SEBS (from SEBS-*g*-MA + AMP) and SMA.

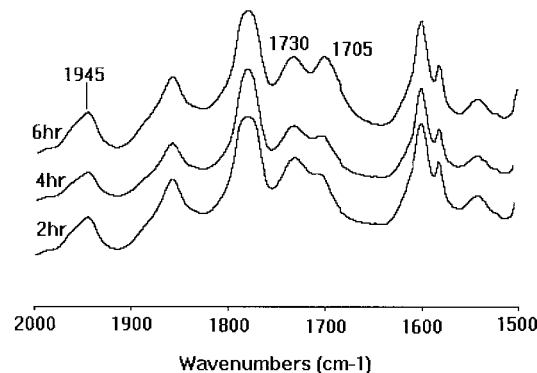


Figure 9 FT-IR spectra of the one-step reaction scheme at various times as depicted in Figure 2.

the reaction scheme 1 (Fig. 1). The FT-IR spectrum of the product obtained in the second stage (Fig. 8), shows the corresponding signals of the imide (1730 cm^{-1}) and carboxylic acid (1705 cm^{-1}) groups, besides the characteristic signals of SEBS-*g*-MA and SMA ($3000\text{--}2800\text{ cm}^{-1}$). It is assumed that the ester group signal is overlapped with the signals of the unreacted maleic anhydride. The compatibilization reaction must proceed, however, as the level of insolubles in this second reaction step climbs to 37.1%. Clearly, the pendent hydroxyl groups of the SEBS material are participating in reactions with the SMA as depicted in Figure 1 (step 2).

The progress of a one-step compatibilization reaction where the SEBS-*g*-MA, AMP, and SMA materials are combined simultaneously (Fig. 2) was also followed by FT-IR spectroscopy (Fig. 9). It can be noticed that the imide group is formed during the first hour of reaction (1730 cm^{-1}). Two hours later the signal at 1705 cm^{-1} , corresponding to the carbonyl group of the carboxylic acid appears, and it continues to growing until 6 h after reaction, leading to a 1 : 1 relationship in respect to the imide signal. This fact indicates that the alcohol group of the AMP reacts (2 h later) producing the ester (overlapped with maleic anhydride signals) and the carboxylic acid groups. At this moment, the compatibilized product (SMA-SEBS-*g*-MA) [Fig. 2(c)] is formed as well as the self-crosslinked products SMA-SMA [Fig. 2(d)] and SEBS-*g*-MA-SEBS-*g*-MA [Fig. 2(b)]. The relative concentration of the preceding three products is random, although, a higher concentration of SMA-SMA crosslinked material could be expected according to the higher reaction rate observed with the SMA copolymer (one-step reaction).

Comparing the one-step reaction with the two-step reaction, it can be observed that in the first (Fig. 9), both the imide and the carboxylic acid are formed from the beginning because of the high concentration of maleic anhydride contained on SMA copolymer. The high MA concentration increases the reaction velocity, but it produces a highly crosslinked system. The insoluble material determined for the one-step reaction was 43.2 wt %. This value is comparable to that observed in the two-step reaction scheme; however, the controlled formation of hydroxyl functionalized SEBS, which in turn, react with SMA is highly unlikely in this one-step process.

SEBS-*g*-MA must first react with AMP before 4 h of reaction time, and then with SMA, to obtain a higher concentration of the SMA-SEBS-*g*-MA compatibilized product. Longer reaction times (6–8 h) could lead to a higher concentration of SMA-SMA crosslinked material because of the higher concentration of MA in the SMA copolymer. However, the gel formation was not controlled in the material used for this study. To control the gel formation, it would be necessary to compatibilize SEBS-*g*-MA and SMA copolymers with much lower molecular weights and MA concentrations.

CONCLUSIONS

A hydroxyl functionalized SEBS is obtained when maleated SEBS is reacted with AMP (hydroxyl amine-functionalized monomer). Self-crosslinking is limited, due to the rapid consumption of the MA moieties by the primary amine groups. In a second step, the compatibilization reactions between the hydroxyl functionalized SEBS and SMA were carried out. The OH—MA coupling reaction was evident from the high degree of insolubles formed. The work presents a unique reaction pathway for the generation of hydroxyl functionalized SEBS materials. These compatibilization agents are expected to have utility in a range of applications in which the hydroxyl functionality could be exploited.

From FT-IR and NMR analysis, coupling reac-

tions were shown to proceed via the well-understood procedure of amine/anhydride and hydroxyl/anhydride reactions. Monomer–monomer analogue reactions aided to the identification of the various carbonyl groups formed during the progress of polymer–polymer compatibilization steps. From these reactions, it was found that crosslinking of the SEBS system can be controlled because the hydroxyl group is by far less reactive than the primary amine group.

The authors wish to thank the Mexican National Council of Science and Technology (CONACyT) for the financial support of this work and the grant given to Ms. D. Zaragoza-Contreras. We also wish to thank to Dr. Donald Weinkauff for his helpful and valuable advice.

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