Functionalization of Styrene–Butadiene–Styrene (SBS) Triblock Copolymer with Glycidyl Methacrylate (GMA)

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ABSTRACT: A styrene–butadiene–styrene triblock copolymer (SBS) was functionalized with glycidyl methacrylate (GMA). Grafting reactions were carried out in an internal mixer at 170°C, using dicumyl peroxide (DCP) as an initiator. The effect of three variables, % GMA, % DCP, and reaction time, on grafting were studied using a factorial design to analyze the experimental data. GMA was grafted onto SBS and its incorporation increased with the % GMA added. The factors levels studied indicated that was an optimum % DCP point about 0.1% w/w to achieve the best incorporation and conversion values. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 2074–2079, 2003

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INTRODUCTION

The commercial importance of toughened polymer blends has rapidly increased in the last years. Blending of two or more polymers allows one to modify the thermoplastic properties, obtaining new engineering materials. The aim of these blends can be, for example, to improve the properties of commodity thermoplastics or to lower the cost of engineering high-performance polymers. However, most blends are immiscible and often have poor mechanical properties and unstable morphology. Especially, the impact toughness is often poor due to the immiscibility and lack of interfacial adhesion between the polymer phases. Addition of suitable block or graft copolymers as compatibilizers for such immiscible polymer blends is thus necessary to improve the compatibility and blend properties.[1,2]

An important class of blends is that of thermoplastics with elastomers. The toughness of most thermoplastic polymers can be considerably enhanced by the incorporation of a dispersed rubbery phase. The toughening mechanisms are influenced by the properties of the matrix material and by the morphology of the blend.[1,2]

Thermoplastic elastomers or rubbers, such as the ethylene–propylene copolymer (EPR), styrene–(ethylene–butylene)–styrene triblock copolymer (SEBS),[3] or styrene–butadiene–styrene triblock copolymer (SBS), have been used to toughen semicrystalline polymers such as nylon 6. However, blends of nylon with rubbers may not be tough because the rubber particles formed during melt blending are too large and adhesion may not be adequate.[4] This fact creates the need of using a compatibilizer to increase adhesion between the phases. Usually, the compatibilizer is the same elastomer grafted with a reactive group. This grafted group is reactive toward end groups of the thermoplastic continuous polymer phase of the blend, while the elastomeric main chain of the compatibilizer is soluble and entangled with the elastomer phase.[5]

Maleic anhydride (MAH), maleic acid (MA), dibutyl maleate (DBM), and acrylic acid (AA) and its esters are the main grafting monomers used in the chemical modification of the elastomers. The glycidyl methacrylate (GMA) epoxide group reacts with both electrophiles and nucleophiles,[6] providing versatility in reactive compatibilization. GMA has been used as a grafting monomer onto polyolefins to compatibilize polymer alloys such as polyolefins/nylon or polyolefins/polyesters because epoxy groups of GMA can react with —OH, —COOH, and —NH₂.[4] GMA was also grafted onto the surface of ultrahigh modulus polyethylene (UHMPE) fiber to improve the wettability and adhesion.[7] GMA was grafted onto polypropylene (PP) using peroxide initiators and the resulting material has been used in the reactive compatibilization of PP blends with nitrile rubbers.[8] Blends of nylon 6 with SBS-g-MAH[9] have been obtained to improve the impact properties of nylon. SBS, SEBS,[10] or EPR[11]

containing maleic anhydride or epoxy functionalities have been effective in improving the properties of nylon blends.

Because SBS is more susceptible to crosslinking then are saturated elastomers, like EPR and SEBS, the majority of the literature related to elastomer functionalization reactions take into account only the functionalization of saturated elastomers, although the functionalization of SBS, comparatively to SEBS, has the advantage of avoiding the hydrogenation process. Consequently, it becomes very useful to establish the reaction conditions that allow one to maximize the monomer incorporation/crosslinking relation. In this way, statistical tools, like factorial design, are very useful in order to analyze the influence of the different factors that can affect the reaction performance. Maurano et al.[12] used factorial design to study the functionalization of SBS with MA, finding the optimal conditions for this system. The purpose of this work was to study the melt functionalization of SBS with GMA in a mixer and to use factorial design to evaluate the influence of GMA and peroxide content on the grafting degree, conversion, and crosslinking.

EXPERIMENTAL

Materials

SBS (M_n = 88,000, M_w = 119,000, styrene/butadiene = 16.4/83.6 mol %) was supplied by Petroflex Ind & Com Ltda. GMA (Aldrich Chemical Co., Inc.) and dicumyl peroxide 98% (DCP) (Aldrich Chemical Co., Inc.) were of analytical grade.

Grafting reactions

The grafting of SBS with GMA was carried out in a Haake Rheomix 600 internal mixer, equipped with a
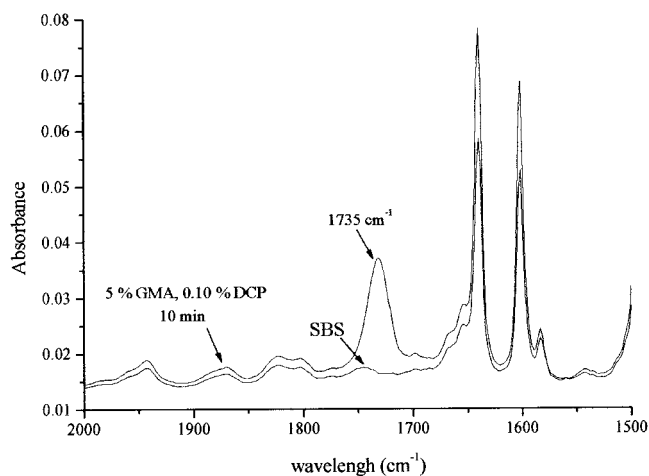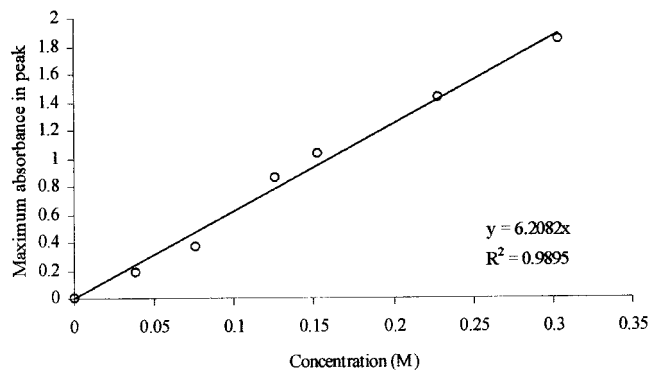
Figure 2 Calibration curve to determine the grafting degree.

pair of high-shear rolled-type rotors. The mixer chamber was initially heated to 170°C and saturated with argon. The rotor was set at a speed of 40 rpm and SBS was introduced into the chamber. After 2 min, GMA and DCP were added and the graft reaction was continued for a predetermined time. The torque change with time was monitored during the reaction. Removal of nonreacted GMA and DCP was accomplished by dissolving the reaction product in chloroform for 3 h and then precipitating the grafted SBS into ethanol under continuous stirring. The purified grafted SBS was filtered and dried overnight in a vacuum oven. About 2 g of the purified product were extracted with toluene in Soxhlet extractor for 48 h to separate the insoluble fractions.

Characterization

The grafting degree of SBS-*g*-GMA samples was determined by infrared spectra employing thin films (50–100 μm). The absorbance of the carbonyl group at 1735 cm^{-1} was used to determine the GMA concentration in the sample by using a calibration curve of absorbance versus GMA concentration. Absorbance values were determined by baseline correction. The calibration curve was obtained from solutions of GMA in chloroform. All infrared measurements were performed on a Bomem MB 102 FTIR spectrophotometer. Films were molded at 170°C, under 5 ton/cm^2, for 2 min.

FTIR spectra of SBS and SBS-*g*-GMA films are shown in Figure 1. The increase of the absorption band at 1735 cm^{-1} demonstrated the occurrence of the grafting reaction, since this band is characteristic of the carbonyl group in the GMA molecule.

The concentration of GMA groups in SBS-*g*-GMA films (C_{GMA}) was determined using a calibration curve obtained from the absorbance of the GMA C=O group. This calibration curve, obtained from solutions of GMA in chloroform, is shown in Figure 2. Good cor-
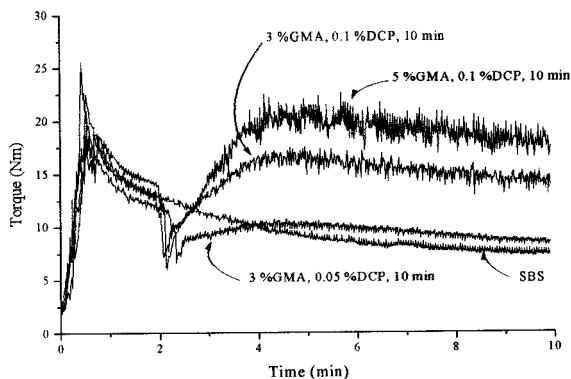
Figure 1 IR spectrum of SBS and grafted SBS with GMA (5% GMA, 0.1% DCP, 10 min).

Figure 3 Torque curves of grafting onto SBS.

relation ($R = 0.995$) among the data was achieved and the linear relation was used as the calibration curve. As nongrafted SBS presents a low-intensity absorption at 1735 cm^{-1} (Fig. 1) and the thickness of films used in the FTIR analysis varies from sample to sample, the absorbance A_{GMA} used in the calculation of C_{GMA} is given by

$$A_{GMA} = A_{SBS\text{-}g\text{-}GMA} \frac{b_{ref}}{b_{SBS\text{-}g\text{-}GMA}} - A_{ref}$$

where $A_{SBS\text{-}g\text{-}GMA}$ and $b_{SBS\text{-}g\text{-}GMA}$ are the absorbance at 1735 cm^{-1} and the thickness of SBS-g-GMA films, respectively. A_{ref} and b_{ref} are the absorbance at 1735 cm^{-1} and the thickness of the nongrafted SBS used as a reference, respectively. The grafting degree was calculated as

$$GD\ (\%) = \frac{C_{GMA}}{(C_{GMA} + C_{RU})} \times 100$$

where C_{GMA} is the concentration of GMA obtained from the calibration curve and C_{RU} is the concentration of repetitive units in the SBS film.

^{1}H-NMR was used to determine the composition of SBS using a Varian VXR 300-MHz spectrometer. The composition of SBS is 16.5% units of styrene, 66.8% units of 1,4-butadiene, and 16.7% units of 1,2-butadiene.

Experimental design

Experimental design concepts were discussed in various references.[13–15] The two major advantages of using a statistically based design are that interaction effects can be analyzed and precision information can be more easily obtained with fewer experiments.

In this work, three factors of a two-level factorial design (2^3) were used to study the grafting reaction of GMA onto SBS. The three factors were the reaction time, GMA, and peroxide concentrations. All the possible factor and level combinations were run, resulting in eight experiments. The effects of the three factors on the grafting degree, conversion, and torque were analyzed. On the basis of the analysis of the results of this first set of eight reactions, a complementary set of four reactions was executed to verify the tendencies indicated by the factorial analysis.

RESULTS AND DISCUSSION

Torque–time behavior

The torque–time curve of pure SBS, presented in Figure 3, was characterized by an initial sharp peak due to the material loading followed by a zone of decreasing torque. Torque–time curves for the functionalization reactions showed five characteristic zones: (1)

TABLE I
Grafting Reactions of GMA onto SBS (First Reaction Set)

|	Factors and levels			Results			
Entry	GMA (wt %)	Reaction time (min)	DCP (wt %)	Grafting degree (mol%)	Grafting degree (wt %)	Conversion (%)	Final torque (Nm)
1	—	—	—	—	—	—	7.2
2	—	10	0.10	—	—	—	6.6
3	5.0	10	—	0.04	0.09	1.77	1.7
4	3.0	7	0.05	0.07	0.16	5.36	8.4
5	5.0	7	0.05	0.12	0.28	5.59	10.2
6	3.0	10	0.05	0.09	0.20	6.60	8.2
7	5.0	10	0.05	0.17	0.38	7.55	9.5
8	3.0	7	0.10	0.11	0.26	8.68	15.8
9	5.0	7	0.10	0.21	0.47	9.41	17.0
10	3.0	10	0.10	0.17	0.39	13.03	14.6
11	5.0	10	0.10	0.38	0.87	17.42	17.6

40 rpm, 170°C.
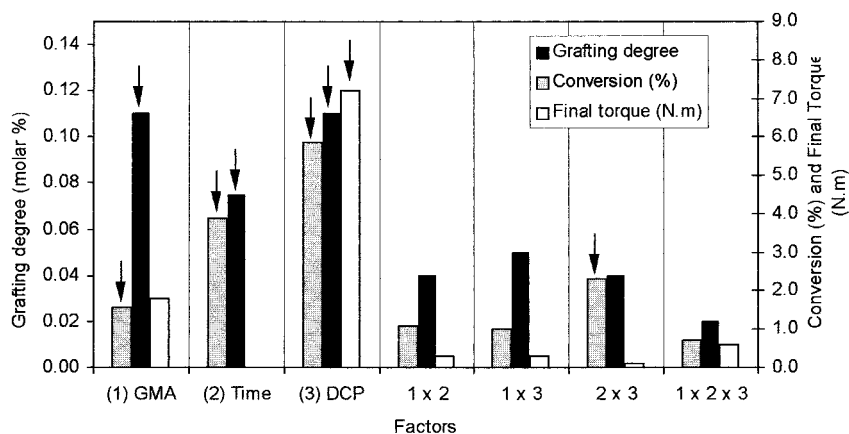
Figure 4 Principal and interaction effects on grafting degree, conversion, and crosslinling.

initial sharp peak due to the material loading; (2) initial decrease of torque due to the material melting; (3) sharp decrease of torque due to the mixer opening (for the addition of the GMA and DCP mixture); (4) increase of torque attributed to the grafting reaction and, probably, to some crosslinking reactions by free radicals leading to microgel formation, and (5) a plateau region of nearly constant torque. The final torque is directly related to the viscosity that depends on the molecular weight, polydispersion, and degree of crosslinking. Data in Table I and Figure 3 show that grafting and torque are strongly influenced by the reaction conditions.

Analysis of the experimental design results

Table I presents the first reaction set of the grafting of GMA onto SBS. The values of the final torque represent the value registered of the torque by the mixer at end of the each reaction. Grafting degree values were calculated as the ratio between the molar concentration of grafted GMA and the total molar concentration in the system (molar concentration of repetitive units plus molar concentration of GMA). Conversion represents the ratio between the amount of grafted GMA and the total amount of GMA added to the reaction system. The presence of peroxide only (entry 2) did

not change the final torque, indicating the absence of crosslinking. A small amount of GMA was incorporated without the presence of DCP (entry 3), probably due to radical formation through shear stress and thermal degradation. The decrease in final torque was caused by the unreacted GMA that acted as a plasticizer.

The factors, that is, the controlled variables considered in the 2^3 factorial design and their levels are summarized in entries 4–11 of Table I. The main interaction effects of the three factors considered on these variables were calculated using the characteristic design matrix[13] and data of Table I.

The effects of each factor were calculated and Figure 4 presents these effects on the grafting degree, conversion, and torque (responses). The first three sets of bar graphs (Fig. 4) show the main effects of each considered factor. Second- and third-order interaction effects are shown from the third to the seventh set of bar graphs. Then, for example, the sets of bar graphs indicated by 2 × 3 and 1 × 2 × 3 represent the second-order interaction effect between factors 2 (time) and 3 (DCP) and the third-order interaction effect, respectively. A significant positive or negative effect of a factor on a response indicates the appropriate changes in the factor levels to reach the optimization. Significant effects were pointed out in Figure 4 by

TABLE II
Second Set of Reactions: Reaction Parameters and Results

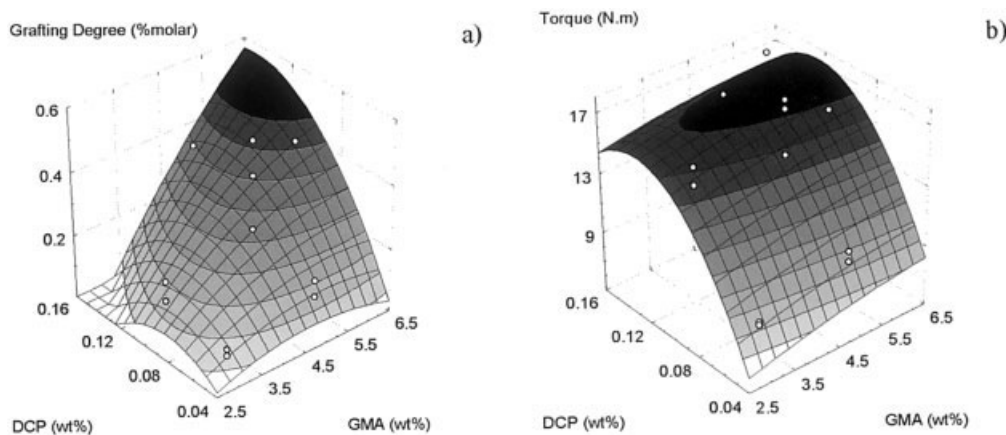|	Parameters of reaction			Results			
Entry	GMA (wt %)	DCP (wt %)	Reaction time (min)	Grafting degree (mol %)	Grafting degree (wt %)	Conversion (%)	Final torque (Nm)
1	5.0	0.15	10	0.36	0.82	16.41	15.6
2	6.0	0.10	10	0.43	0.99	16.56	15.7
3	5.0	0.10	12	0.49	1.12	22.30	14.0
4	6.0	0.15	12	—	—	—	17.2

40 rpm, 170°C.

Figure 5 Effect of % DCP and % GMA on (a) grafting degree and (b) final torque.

means of vertical arrows placed above the corresponding bar.

The % GMA exerted a positive effect on the grafting degree, but did not exert a significant effect on conversion and torque. The reaction time presented a positive effect on the conversion and grafting degree. The positive effect of DCP content (% DCP) on the grafting degree was related to the increase of the amount of free radicals in the reaction medium with its increase. On the other hand, the increase of GMA content (% GMA) leads to higher grafting degrees due to the higher probability of a free radical reacting with a GMA molecule before being terminated by the collapse with another free radical. The difference among the effects on the grafting degree and conversion can be explained by the low values of conversion obtained in the experiments. The maximum value of conversion was 17.4%. In these conditions, the grafting degree is more dependent on the GMA content than on conversion.

Other important information that can be extracted from Figure 4 is that the DCP content had a strong positive effect on the final torque. This fact indicated that it was not possible to increase the grafting degree without increasing the torque level due to crosslinking reactions in the range of the concentrations analyzed.

The fact that almost all interaction effects were not significant and that all principal effects were positive pointed to the possibility of achieving higher levels of GMA incorporation by increasing the level of the three factors studied. On this basis, a complementary set of reactions was carried out to verify this possibility.

Complementary reactions

Four complementary reactions were carried out. The reaction parameters and the results of these reactions are shown in Table II. When the three factors were increased at the same time, the sample was not soluble

in toluene and it was not possible to measure the grafting degree and conversion. The value of the final torque was not as high as in the other three reactions, and the crosslinking reaction may have continued after removing the sample from the mixer, probably due to the high excess of reagents.

The results of the first set of reactions and the three new points of Table II were used to construct a surface plot for each of the variables considered as a function of the factors that had a significant effect. The surface plot for the grafting degree, final torque, and conversion are shown in Figures 5 and 6.

Figure 5(a) shows that grafting degree increased continuously with the % GMA, and in relation to the % DCP, it reached a maximum point at 0.1%. The increase in torque, shown in Figure 5(b), indicated that higher levels of DCP favored the chain-radical formation and the combination of the two radicals will lead to crosslinking. The increase in % GMA was not enough to avoid the combination reaction. A similar behavior is presented in Figure 6 for conversion as a
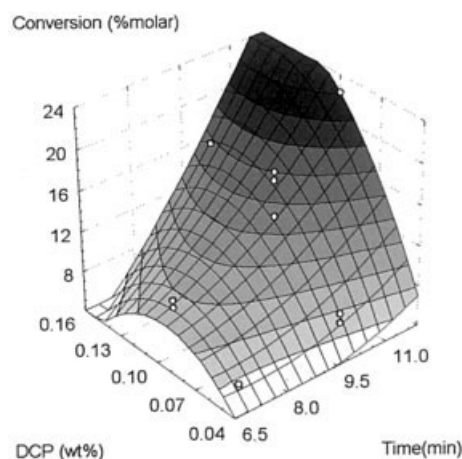

Figure 6 Effect of % DCP and reaction time on conversion.

function of the % DCP and time. Conversion tends to a limit value at high reaction times. Increasing all the factors increased the grafting degree and, moreover, the torque level also increased.

CONCLUSIONS

GMA was grafted onto SBS in the melt. The effect of % GMA, % DCP, and reaction time on the grafting degree, conversion of GMA, and crosslinking were studied using a factorial design. All these factors presented a positive effect on the grafting degree. DCP also presented a strong positive effect on the final torque, indicating that it is not possible to increase the grafting degree without increasing the torque level due to crosslinking reactions in the range of the concentrations analyzed. The factor levels studied indicated that there is an optimum % DCP point about 0.1% w/w in which it is possible to achieve the highest incorporation and conversion values at a low crosslinking level. Above this DCP content, a high number of free radicals will participate in other crosslinking reactions, decreasing the quality of the reaction product.

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