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C. Rosales[a]; H. Rojas[a]; R. Perera[a]; A. Sánchez[a]; M. Vivas[b]
[a] Grupo de Polímeros USB, Departamento de Mecánica, Universidad Simón Bolívar, Caracas, Venezuela [b] Departamento de Química, Instituto Universitario de Tecnología "Dr. Federico Rivero Palacios", Caracas, Venezuela

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C. Rosales,* H. Rojas, R. Perera, and A. Sánchez

Grupo de Polímeros USB
Departamento de Mecánica
Universidad Simón Bolívar
Apartado 89000, Caracas 1080-A, Venezuela

M. Vivas

Departamento de Química
Instituto Universitario de Tecnología “Dr. Federico Rivero Palacios”
Carretera Panamericana Km. 8
Vía Los Teques, Caracas, Venezuela

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ABSTRACT

The chemical modification of two thermoplastic elastomer styrene/ethylene-buthylene/styrene copolymers (SEBS) with diethylmaleate (DEM) as functionalizing agent was carried out in a corotating twin screw extruder and in an internal mixer. The residence time distribution of the extruder was studied due to its great influence on the grafting chemical reaction, the degree of functionalization, and the viscoelastic properties of the obtained modified polymers. The influence of copolymer melt viscosities, and DEM and initiator concentration ratio on the grafting degrees was studied as well. In this case, an internal mixer was used.

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*Author to whom correspondence should be addressed. E-mail: crosales@usb.ve

Optimal processing conditions were established to obtain grafted polymers characterized by good processability and an absence of crosslinking. The grafting degree achieved in the internal mixer was the same for both copolymers with different viscosities and it increased as the DEM and initiator concentrations and concentration ratios were increased.

INTRODUCTION

The development of new materials through immiscible polymer blending implicitly leads to the incorporation of agents that promote or favor the compatibility between the components [1]. The production processes of polymers suitable to be used as compatibilizing agents in those systems could generate additional costs which suggests that quick and economic ways to obtain them should be developed. The functionalization consists in the insertion or incorporation of molecules into the polymer chain, that could act as interfacial agents between the components of incompatible blends, through chemical reactions with one of the polymers [1, 2]. This could be achieved through different processes. One of them is reactive extrusion, which is an important means, not only because it is a continuous process, but because it is possible to use conventional processing equipment as well.

The use of extruders in the chemical modification and/or in reactive blending of polymers is known as reactive extrusion. Maleic anhydride grafted polypropylene (PP-*f*-MA), styrene/ethylene-buthylene/styrene copolymer (SEBS-*f*-MA) and ethylene/propylene elastomer (EPR-*f*-MA) are among the most widely used of the modified commercial materials in reactive blending [3]. In reactive extrusion, some inherent parameters such as the residence time distribution, the reactants mixing and dispersion, as well as their diffusion and compatibility, must be taken into consideration and must be controlled. The influence of temperature, mass flow rate and screw speed in the residence time distribution and in the kinetics of decomposition of the initiators employed in the process, should also be considered [4-6].

In articles by Rosales *et al.* [7-8], dealing with solution grafted polyolefins, the influence of temperature, time and functionalizing monomer (diethyl maleate) and initiator (peroxide) concentrations on the grafting degree of an extrusion grade linear low-density polyethylene (LLDPE) was reported. Time and temperature simultaneously influenced the kinetics of the peroxide decomposition and furthermore, the grafting degree obtained was a function of the amount of dissociated initiator. On the other hand, the grafting degree increased with the initiator and monomer concentrations. Particularly, when the initiator concentration was increased, a limiting value of the grafting degree was achieved because when higher free radical concentrations are generated, they recombine at higher speeds.

In functionalization via extrusion, a similar trend (concerning the influence of initiator and monomer concentration) was found for LLDPE. Additionally, the influence of variables such as the screw configuration of a corotating twin-screw extruder, the monomer and initiator feeding method, the type of polyethylene where the monomer was to be grafted, that is, high, low and linear low-density polyethylene, on the grafting degree and on the molecular characteristics of the functionalized product was studied. Furthermore, the rheological and thermal propertiesof these materials were determined. It was also reported that the residence time distribution in the extruder is a fundamental parameter in the functionalization reaction, and that the initiator incorporation when the monomer is well mixed in the molten polymer, avoids the formation of gels in the functionalized product, at the experimental conditions tested [9].

The grafting degree is a function of the virgin material viscosity in the elements of the extruder screw, that is, the higher the viscosity, thelower the grafting. Even though the functionalization slightly modifies the molecular characteristics of the obtained products, the rheological properties change largely and are proportional to the grafting degree. This behavior is attributable to the secondary reactions that take place as well in the process [10-12].

This article reports on the chemical modification via extrusion of the thermoplastic elastomer styrene/ethylene-buthylene/styrene (SEBS) with diethyl maleate (DEM) as the functionalizing agent or monomer. The residence time distribution curve of a corotating twin-screw extruder is determined as a fundamental parameter in the chemical reaction. The influence of that distribution in the grafting degree and in the obtained viscoelastic properties of the chemically modified materials is also studied. In an internal mixer, the influence of the ratio of functionalizing agent to initiator concentration and of the viscosity of two different copolymers on the grafting degree is established. It is important to note, at this point, that DEM was used in previous works of polyolefin grafting; however, it has not yet been employed in the functionalization of the triblock copolymer SEBS.

EXPERIMENTAL

Materials

Two styrene/ethylene-buthylene/styrene copolymers, SEBS 1650 (SEBS1) and SEBS 1652 (SEBS2), supplied by Shell Chemical Company, with an styrene/rubber ratio of 29/71 and Brookfield viscosities in toluene of 8 and 1.35 Pa.s, respectively, were used.

Diethyl maleate (DEM) and dicumyl peroxide (DCP), both laboratory reagent grade, were employed as the functionalization monomer and initiator, respectively, and used as received. In the poly(diethyl fumarate) (PDEF) synthesis, diethyl fumarate and azo-bis-isobutironitrile (AIBN) were used. Dibu-thyl maleate (DBM) and a linear low-density polyethylene were employed in order to establish the residence time distribution (RTD) of the polymers in the extruder at the functionalization conditions.

Functionalization in the Internal Mixer (Rheomix)

In order to perform the functionalization of the SEBS, an internal mixer or Rheomix made by Haake was employed. The reaction was carried out at 200°C, in batches of 40 g (an 80% of the mixer capacity). Table 1 shows the composition of the batches.

The SEBS was fed in the Rheomix and nitrogen gas was used during the reaction to evacuate the oxygen. The frequency of the rotors was set at 30 rpm and the SEBS was mixed during two minutes. At that moment, the 60% of the total volume of DEM was added and mixed for eight minutes at the same frequency. Then, the frequency was raised at 60 rpm, the system was again purged with nitrogen gas and a mixture of the initiator and remaining DEM was fed in the equipment and mixed for ten more minutes. Finally, the product was discharged.

Functionalization in the Extruder

In reactive extrusion, a Berstorff ECS-25 corotating intermeshing twin screw extruder was used. Figure 1 shows the screw configuration. The screw was assembled from individual screw elements: A, B and F were conveying elements, C, D and G kneading mixing elements, E was a mixing gear and H a blister element to avoid the liquid set back.

The grafting process comprised two stages. Both were carried out at 35 rpm and at a die temperature of 238°C. In a first stage, a premix of 80% of

TABLE 1. Functionalizing Monomer (DEM) and Initiator (DCP) Concentration in phr of SEBS

Material	DEM (phr)	Initiator (phr)	Equipment Used
SEBS1-*fR*-DEM	35	1.25	Internal Mixer (Rheomix)
SEBS2-*fR*1-DEM	10	0.50	Internal Mixer (Rheomix)
SEBS2-*fR*2-DEM	35	1.25	Internal Mixer (Rheomix)
SEBS1-*fE*-DEM	10	0.50	Twin-screw extruder (Berstorff ECS-25)
SEBS2-*fE*-DEM	10	0.50	Twin-screw extruder (Berstorff ECS-25)

the total volume of DEM in the SEBS copolymer was made. In the second stage, the product from the first stage and a mixture of DCP and the remaining DEM was extruded at a mass flow rate of 0.4 Kg/h. Both, monomer and initiator, were fed in the extruder third feed port (Figure 1), because at that point isothermal conditions and the complete melting of the SEBS were already achieved.

The functionalization in the extruder was performed with a total of 10 phr of DEM and 0.5 phr of DCP. A maximum of 10 phr of DEM was used in thegrafting due to the migration effect that arise from SEBS/DEM incompatibility. Functionalization results from the internal mixer were considered to carry out the reactive extrusion process. Acceptable grafting degrees were obtained there at such monomerand initiator levels. At this point, it is worth noting that the reactive extrusion of the SEBS 1652 could exclusively be accomplished, because the SEBS 1650 had a very high viscosity and no processing conditions could be found that avoided degradation problems.

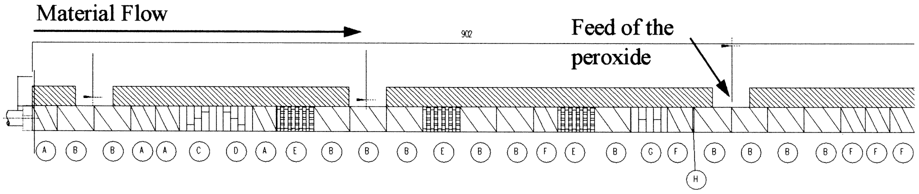

Figure 1. Screw configuration of the Berstorff ECS-25 corotating twin-screw extruder.

Residence Time Distribution Experiments

Reactive extrusion is a process where extruders are used as chemical reactors. The particles that enter the extruder at the same time, do not leave it at the same time, that is, a distribution of residencetimes is thus generated. Consequently, the mean residence time of the reactants inside the extruder is a very important process variable because it is considered, to a first approximation, as the reaction time. The residence time distribution function describes the history of the polymer and reactants inside the extruder and it is reflected in the efficiency or yield of a chemical reaction and in the extent of degradation. From expressions in the literature, the mean residence time (t_m) and the amount of material that has left the extruder at that particular time can be calculated [4].

In RTD experiments, LLDPE was fed to the extruder at 35 rpm, 200°C and at a mass flow rate of 0.4 Kg/h. Dibuthyl maleate was used as tracer because its boiling point is higher than that of DEM, so evaporation losses were minimized. It was added as a pulse through the liquid injection zone (Figure 1). Extrudate samples were collected afterwards at several intervals of time and analyzed by Fourier Transformed Infrared Spectroscopy (FTIR), using a Nicolet Magna 550 Spectrophotometer. Each experiment was repeated twice.

Synthesis of Poly(diethyl fumarate)

Poly(diethyl fumarate) was prepared in order to obtain a calibration curve to estimate the grafting degree of the SEBS. The repetitive unit of the PDEF is very similar to the grafted groups in the SEBS. The PDEF was synthesized by free radical polymerization of diethyl fumarate monomer. The latter was purified by vacuum distillation at 133°C and 25 mm Hg. Afterwards, 75.15 g of it were placed in a round bottom two-necked flask with 1.20 g of AIBN as a free radical initiator. Nitrogen gas was used as an inert atmosphere.

The monomer and initiator solution was heated to 70-75°C during 7 hours under nitrogen atmosphere andconstant stirring. A viscous solution was obtained and poured little by little in petroleum ether. As the polymer precipitated, it was taken out of the ether with an spatula. A new portion of petroleum ether was used each time that the polymer precipitation became difficult, due to a saturation of the ether with umpolymerized monomer.

The polymer thus separated still contained an important amount of monomer, so its complete purification was achieved by further dissolution in ethylacetate and subsequentprecipitation in petroleum ether. The PDEF was finally dried in a vacuum oven at 35°C for 16 hours.

Analysis of the Grafted Products

In order to eliminate the residual monomer or DEM from the functionalized product, 20 g of it were dissolved in 300 mL of dichlorobenzene at 120°C. Then, the polymer was precipitated in 600 mL of methanol and dried in a vacuum oven at 70°C for 15 hours. The resultant material was then dissolved in 300 mL of n-heptane at 120°C to verify the absence of crosslinked material by visual examination. Finally, the n-heptane was evaporated.

Three films of each grafted SEBS thus washed were compression molded at 170°C. On the other hand, blends of SEBS and PDEF were made in solution at different compositions using toluene. A small amount of each were deposited on KBr windows and kept at room temperature until the partial evaporation of the solvent. The KBr windows were finally dried in a vacuum oven at 35°C for 24 hours. Each blend was prepared twice and was used in the construction of the calibration curve.

IR spectra of the blends and unmodified and grafted SEBSs were obtained using a Nicolet Magna 750 FTIR Spectrophotometer. The materials were analyzed in the range 4000 to 500 cm^{-1} at a resolution of 4 cm^{-1}. The spectra of the blends and grafted SEBS showed a band at 1736-1737 cm^{-1} characteristic of the carbonyl groups in the PDEF and grafted DEM. The peak area at 1736 cm^{-1} and at 1601cm^{-1}, the latter characteristic of styrene in the SEBS copolymer, were measured. The peak area ratios of 1736 cm^{-1}/1601 cm^{-1} were analyzed in order to eliminate the dependence of the carbonyl peak area on the film thickness.

Rheological Properties

The rheological properties of virgin samples of SEBS 1652 and its functionalized products were measured at 200 and 230°C in a Rheometrics RDA-II rheometer using a 25 mm diameter parallel plates. In order to examine the thermal stability of the samples, time sweeps were performed at a fixed strain and at three different frequencies of 0.1, 0.5, and 1rad/s. The frequency sweeps were conducted from 1 to 100 rad/s. All the dynamic properties were determined in the linear viscoelastic range of strain. The total time for loading, trimming and relaxing never exceeded 5 minutes.

Steady state capillary flow properties at higher strain rates were measured at 230°C using a Göttfert capillary rheometer Rheograph, Model 2000. A cylindrical capillary of length-to-diameter ratio of 20 mm/1 mm was employed.

RESULTS AND DISCUSSION

Residence Time Distribution

The chemical modification of polymers through conventional processing methods, such as reactive extrusion, has the advantage over the discontinuous polymerization processes, either in bulk or in solution, that the associated costs are lower in the former. The important variables of the functionalization reaction in the internal mixer (Rheomix) to be taken into consideration are the temperature, which was kept constant during the reaction because a low rotor speed was chosen, and the reaction time (10 minutes). However, in the functionalization during extrusion, other variables such as the mass flow rate, the screw speed, the temperature, which is not uniform in the process, the RTD of the material in the extruder and the screw configuration must be considered.

The RTD curve at the extrusion conditions of 35 rpm and 200 °C and at a mass flow rate of 0.4 Kg/h is shown in Figure 2. It is evident there that the material did not start to exit the extruder until an elapsed time of 306 s., a fact that is related to the time that the material remained in the feed element of the

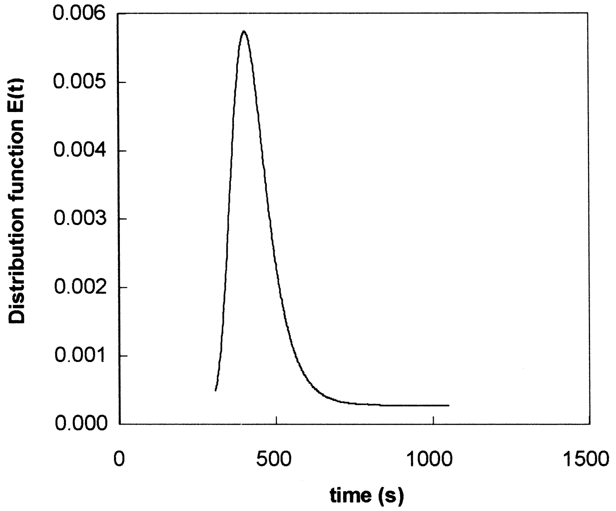

Figure 2. Residence time distribution of Berstorff ECS-25 corotating twin-screw extruder at a mass flow rate of 0.4 kg/h, 35 rpm and 200°C.

extruder. That same time also influences the diffusion of the low-viscosity liquids into the high-viscosity polymeric material and the secondary reactions that take place, such as thermo-oxidative degradation, which in turn lowers the functionalization degree [10].

The material fractions with longer residence times (at the tail of the distribution) are more likely to undergo degradation inside the extruder. The mean residence time and the fraction of material that has left the extruder at the mean residence time at the extrusion conditions employed, were 484 seconds and 69%, respectively, which shows that the initiator decomposition was accomplished completely, because the time calculated to decompose the 99% of initiator was 8 seconds. Even though the temperature and the material used in the RTD experiments were different from those used in the grafting process (200°C and LLDPE), it has been demonstrated elsewhere that the temperature does not influence that distribution at all [4].

The average degree of fill of the screw elements, at the experimental conditions, is another variable that has to be taken into consideration in reactive extrusion in absence of an inert atmosphere (nitrogen). It is calculated from the average holdup value (volume of material in the extruder at the mean residence time) and the free volume of the screw elements downstream from the feed port [4]. Lower degrees of fill allow the presence of air in the screw elements, which in turn promotes thermo-oxidative degradation of the material. The average degree of fill from the peroxide feed port at the extrusion conditions was 95%. On the other hand, the peroxide feed port was open to the atmosphere (Figure 1), with the consequent entrance of air into the extruder. There was also a high transport delay time in the RTD (306 seconds). All those conditions promote secondary reactions (degradation) during the grafting process.

Another variable to be taken into consideration in the chemical reaction of functionalization is the initiator half life at the processing temperature. In the decomposition of the dicumyl peroxide, a free radical reaction with a first order kinetics at 230°C was considered [5,6]. The constants employed to calculate the time needed to decompose 99% of the DCP at 230°C were those reported for the decomposition of the same peroxide in polyethylene and not those reported in mineral oil, because the SEBS to be grafted was a very high-viscosity polymer, which had a polyolefinic block (ethylene-buthylene) in its structure [6]. Thus, the calculated times needed to decompose 99% of DCP in polyethylene were 82 seconds at 200°C and 8 seconds at 230°C.

SEBS Functionalization

To estimate the grafting degree, defined as the ratio of number of DEM moles grafted in the polyolefinic chain of the SEBS per hundred of SEBS moles, or as the weight of DEM units grafted per hundred grams of SEBS, it is mandatory to use calibration curves. The selected method to build those curves is similar to that reported by Fodor *et al.* [13] and Aglietto *et al.* [2], even though the best approach would be to determine the grafting degree from ^{1}H NMR [1].

Solutions of SEBS and poly(diethyl fumarate) were prepared in toluene. The PDEF has ester groups equivalent to those of DEM in the polyolefinic chain of SEBS. In Figure 3, results of area ratios of the carbonyl group band in PDEF ($A_{1736cm-1}$) and of the styrene band in SEBS ($A_{1601cm-1}$) as a function of weight percent of PDEF/SEBS are shown. Since a band at 1736 cm^{-1} is present in SEBS, which is attributed to monosubstituted aromatic groups, its area was subtracted in the making of the calibration curve. Consequently, the curve departs from 0. The linear correlation coefficient obtained for that calibration curve was 0.99.

Most of the reported work on functionalization has been conducted with maleic anhydride as the grafting monomer. This monomer produces homopolymers at the temperatures usually employed as reaction conditions. With the same monomer, the initiator concentration range mostly used goes from 0.03 to 2 phr of polymer. Many of the researchers found that initiator concentrations higher than 1.6 phr promotes crosslinking in LLDPE [2, 14].

On the other hand, monomer concentrations and reaction temperatures most commonly employed go from 1 to 35 phr, and from 140 to 230ºC, respec-

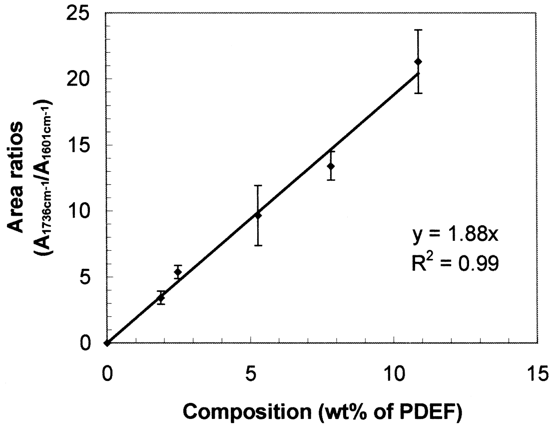

Figure 3. Calibration curve poly(diethyl fumarate)/SEBS blends.

tively. In a research carried out by Ganzeveld and Janssen [14], where dibenzoyl peroxide was used as initiator in the reactive extrusion of HDPE in a temperature range between 160 and 220ºC, it was found that initiator concentrations above 1.6 phr promoted secondary reactions such as crosslinking and that the conversion maximum was achieved at temperatures between 190 and 215ºC.

Diethyl maleate was used as the grafting monomer due to its unsaturated structure and non-homopolymerizable character under the grafting conditions employed. The mechanism ofthe reaction of DEM and polyethylenes has previously been investigated [2, 15] to be based on the initial formation of free radicals from the thermal decomposition of DCP which generates macroradicals by hydrogen abstraction from the macromolecules. Due to the enhanced reactivity of the DEM double bond, macroradicals quickly react with the unsaturated substrate (DEM), while chain propagation is promptly interrupted by transfer with the polyolefin chains. Indeed, ^{13}C NMR spectra of the functionalized polyolefins demonstrated that the side chains in the final product mostly contain one unit of DEM only. Thus, this reaction grafts very short chains, consisting mainly of a single unit of functional monomer, onto the macromolecular chains. Side reactions such as homopolymerization of DEM are to a large extent or totally avoided.

In the reactions with DEM, functionalization takes place more quickly than side reactions, probably due to the molecular structure of DEM. The inductive and resonance effects of two –COOEt groups cause a noticeable charge displacement along the C=C axis, and this displacement makes the unsaturated carbon atoms electron-deficient species. Thanks to this feature these species show enhanced reactivity towards free radicals, and particularly against R-O· alkoxide free radicals with high nucleophilic character, with respect to a non-polar molecule like the polyolefin [2, 15].

The structure of functional groups attached to polyethylene backbones by free radical reactions in solution and in melt have been studied by *Aglietto et al.* [2, 15] and Rojas *et al.* [16]. They have shown that, in the case of functionalization with DEM, the functional groups introduced are almost exclusively diethyl succinate (CH(COOEt)-CH$_2$COOEt).

When DEM has been used in studies of functionalization, either in solution or in melt, researchers have found that in order to obtain a controlled degree of grafting and to avoid secondary reactions such as crosslinking and/or chain scission, DEM/polymer concentration ratios of about 1:1 and temperatures above 200ºC should be used [2, 15]. However, in reactive extrusion, it is very difficult to use such a ratio, because migration of the lower-viscosity DEM, at concentrations above 10 phr, is unavoidable. Hence, thatmaximum DEM concentration of 10 phr was chosen. Furthermore, polymer/initiator ratios between 1.5 and 4.5 have been proven to produce grafting degrees of 23.2 and 25.4 wt%, respectively, in LLDPE, whereas the fractions of non-degraded polymer were 98 and 92 wt%, respectively [2]. Thus, the initiator concentration was chosen bearing in mind that amounts higher than 1.5 wt% promote a high level of crosslinking and/or chain scission in linear polyethylenes and in polypropylenes, respectively [9-12].

Figure 4 shows the IR spectra of SEBS2, both unmodified and grafted. The grafted's spectrum (SEBS2-f-DEM) shows a band at approximately 1736 cm^{-1}, which is much less evident in the pure SEBS (SEBS2). In the first case, it corresponds to the stretching of the carbonyl group (C=O) that comes from the ester group of the DEM grafted into the chemical structure of the SEBS, whereas in the second one, the presence of that band is attributed to monosubstituted aromatic groups and to the carbonyl groups generated by material degradation during processing because the SEBS2 was extruded twice at the same extrusion conditions of the functionalized material.

Table 2 exhibits the area ratios and grafting degrees of all functionalized products obtained at different conditions. The grafting degree was estimated from Figure 3. SEBS1 c orresponds to SEBS 1650, and SEBS2 to SEBS 1652. Both materials were modified in an internal mixer in order to ascertain the best reaction conditions.

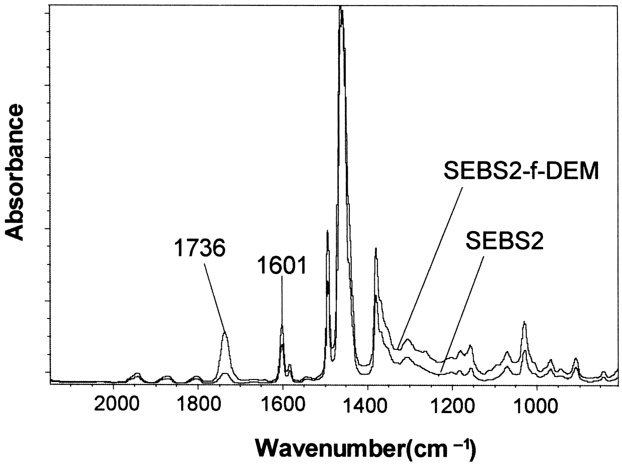

Figure 4. IR Spectra of extruded SEBS2 and functionalized SEBS2 (SEBS2-*f*-DEM).

TABLE 2. Grafting Degrees of Modified SEBSs

Material	Area Ratios ($A_{1736\ cm^{-1}}/A_{1601cm^{-1}}$)	Grafting Degree (wt%)
SEBS1-*fR*-DEM	4.1 ± 0.1	2.2
SEBS2-*fR*1-DEM	2.0 ± 0.1	1.1
SEBS2-*fR*2-DEM	3.9 ± 0.1	2.1
SEBS2-*fE*-DEM	0.74 ± 0.08	0.4
SEBS2 extruded twice	0.40 ± 0.01	-

The relationship between grafting degree and DEM/initiator concentration ratio is directly proportional, be cause as the DEM amount is increased for a given amount of initiator, the effective encounters between the former and the polymer reactive sites are favored, which in turn increase the number of inserted molecules. Furthermore, when the DEM and initiator concentrations are simultaneously increased, there is more dissociated initiator and hence, more reactive sites will be generated. Similar results were found in the grafting of polyethylenes [7, 8].

The obtained results suggest that the grafting degree is independent from the copolymer type at the conditions employed in the internal mixer. However, the low grafting degree achieved in the extrusion functionalized SEBS 1652 is ascribed to the low diffusion of the DEM and/or initiator molecules (low-viscosity liquids) into the high-viscosity polymeric material during the reaction time (or t_m). Another factor that lowers the grafting degree achieved in the extruder is the DEM and/or initiator evaporation losses in the corresponding feed port (open to the atmosphere, Figure 1). On the other hand, the need of higher temperatures to accomplish the processability of SEBS2 in the extruder, the long transport delay time and the fact that the feed port of the extruder is open to the atmosphere, promoted secondary reactions (chain scissions) that lowered the grafting degree.

No mechanisms of the grafting of SEBS with DEM and dicumyl peroxide as the initiator has yet been reported. The main side reactions are different from those reported in linear polyethylenes, because in SEBS, as well as in polypropylene, chain scission takes place, which lowers the molecular weight [12]. Only the SEBS 1652 was functionalized in the twin-screw extruder because the higher Brookfield viscosity of the SEBS 1650 in toluene, due to its higher molecular weight, propitiated its degradation and hindered its modification via extrusion.

TABLE 3. Melt Temperatures and Die Pressures in the Extrusion Process

Material	Melt Temperature (°C)	Die Pressure (kPa)
SEBS1 (first stage)	247 ± 3	9500 ± 2000
SEBS2 (first stage)	241 ± 3	3800 ± 700
SEBS1-*fE*-DEM	feeding problems	dark brown extrusion product
SEBS2-*fE*-DEM	241 ± 3	3100 ± 700

The triblock copolymer of SEBS has a styrene end blocks and a hydrogenated butadiene mid block resembling an ethylene/butylene copolymer. The SEBS was functionalized with DEM onto the hydrocarbon chains. There is a functionalized SEBS with maleic anhidride commercially available, supplied by Shell and designated as Kraton 1901 with the same molecular weight and styrene content of those in the SEBS Kraton 1652. The other SEBS supplied by Shell with lower molecular weight is not hydrogenated (SEBS G-1726X) and therefore a crosslinked structure would be obtained if it were functionalized. Thus, the alternative of using a lower molecular weight copolymer to lower the processing and reaction temperature is not feasible.

Table 3 displays the melt temperature at the die and the die pressure in the extrusion processes. The high melt temperatures obtained are associated to viscous heating at the screw elements due to the copolymers high viscosity. SEBS1, due to its higher viscosity, generates higher viscous heating and die pressure than the SEBS2 does. Thus, the higher temperature and the air at the peroxide feed port promoted thermo-oxidative reactions that made impossible to carry out the functionalization during extrusion of the SEBS1.

In fact, the obtained product of the functionalized SEBS1 showed a dark brown color. It is important to note here that no gels were obtained in the grafted products of this research. However, an extrusion grafted SEBS2 with maleic anhydride made by Chen *et al.* [17] showed the formation of gels and a higher melt viscosity due to the occurrence of crosslinking in the chemical processing.

Rheological Behavior of the Extrusion Grafted Products

In dynamic rheometry tests, the oven heating was achieved in presence of air, which produces degradation at high temperatures. Hence, the sample heating and stabilization and the normal stresses relaxation times prior to the test were controlled and fixed in five minutes (300 seconds). The loss modulus (G”) and storage modulus (G') at frequencies of 0.1 and 0.5 rad/s and at 200 and

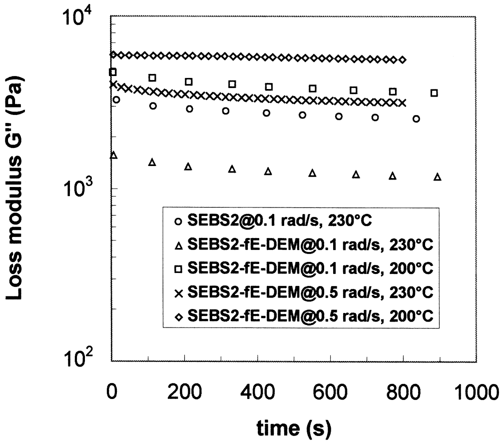

Figure 5. Loss modulus as a function of time for SEBS2 and SEBS2-*fE*-DEM.

230°C, as a function of time, are shown in Figures 5 and 6 for both SEBS2 and extrusion grafted SEBS2 (SEBS2-*fE*-DEM).

Both moduli decreased with time at the temperatures tested due to the thermo-oxidative degradation that took place during the test. The storage modulus showed a more pronounced change because of the stronger influence of the high molecular weight tails of the molecular weight distribution on the material elasticity. In chain scission processes, they decrease in a higher proportion. The influence of the molecular weight on the curves of storage modulus and viscos-

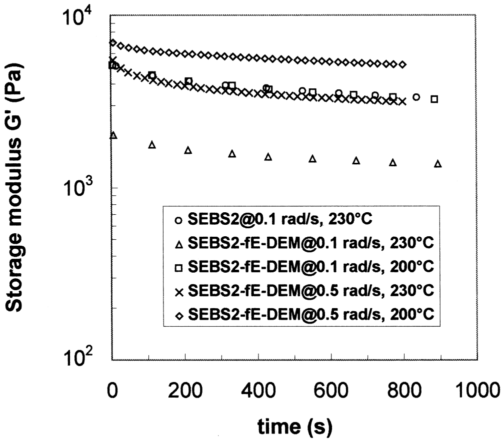

Figure 6. Storage modulus as a function of time for SEBS2 and SEBS2-*fE*-DEM.

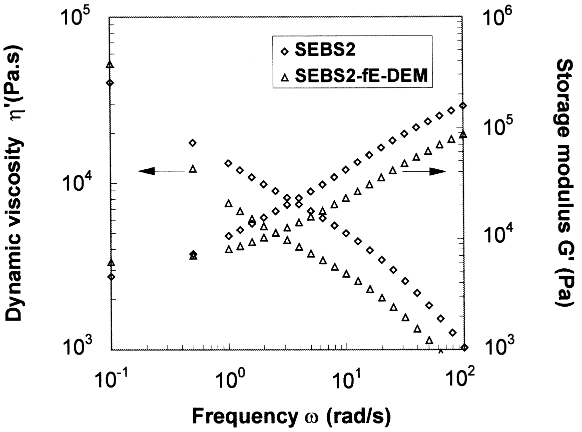

Figure 7. Dynamic viscosity (η') and storage modulus (G') as a function frequency (ω) of the extruded SEBS2 and extrusion functionalized SEBS2-*fE*-DEM.

ity as a function of frequency is more noticeable in the low frequencies region. In the high frequencies range, that influence is weaker [18].

The variation of G' and G" of SEBS2-*fE*-DEM at 0.5 rad/s and 200°C with time up to 300 seconds is lower than 10% and 5%, respectively. Hence, the time never exceeded 600 seconds (including the mounting, trimming and relaxing times) in those tests where the frequency was varied from 1 to 100 rad/s.

Figures 7 and 8 show the dynamic viscosity (=η') and G' as a function of frequency and G' versus G", respectively, for SEBS2 and SEBS2-*fE*-DEM at

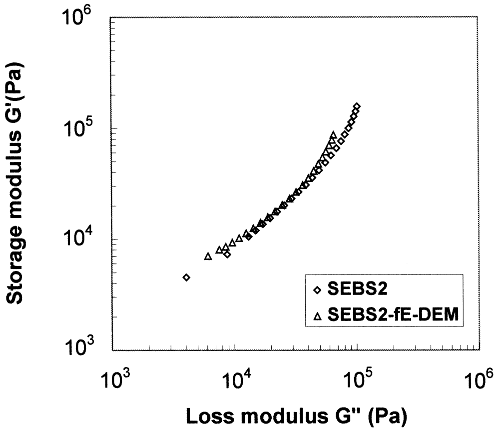

Figure 8. Apparent viscosity (η) as a function of shear rate (γ) for SEBS2 and SEBS2-*fE*-DEM at 230°C.

0°C. G' and G" values at 0.1 and 0.5 rad/s were extrapolated at time 0 (-300 seconds) and are those reported in Figures 7 and 8. When both materials are compared, the SEBS2-*fE*-DEM shows η' and G' vs frequency curves that are displaced towards lower values due to a reduction in its weight average molecular weight through chain scission. However, G' vs G" curves do not show any significant change, because neither the molecular weight nor the temperature affect this type of plots [18]. The form of the curves obtained for both materials reflects their plastic behavior. Since the SEBS is a block copolymer, it has a multiphase structure at a molecular scale at the temperatures tested, because of the incompatibility of the styrene and the ethylene-buthylene blocks [19].

Capillary rheometry of the extrusion functionalized material unfolded a decrease of the apparent viscosity (η) and an enhancement of the critical shear rate (γ_c) where flow instabilities of the polymer appears, when compared to those values in the virgin material (Figure 9). This change is attributed to chain scission in the extruder during the grafting [10-12].

The rheological behavior of the virgin material and its functionalized products at high shear rates can be represented by apower law model. Due to the multiphase structure of SEBSs, the flow curves obtained from the capillary rheometer depended on the employed geometry. Hence, the Cox-Merz Rule [20] is not valid in these materials, that is, the complex viscosities determined from dynamic rheometry and the apparent viscosities determined from capillary rheometry did not match at equal frequencies and shear rates at 230°C.

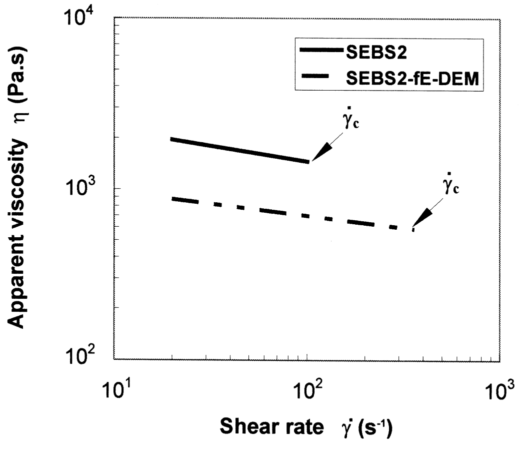

Figure 9. Apparent viscosity (η) as a function of shear rate ($\dot{\gamma}$) for SEBS2 and SEBS2-*fE*-DEM at 230°C.

CONCLUSION

The grafting of DEM into the SEBS copolymers can be achieved in reactive extrusion using a corotating twin-screw extruder if the inherent variables of the process are controlled. The higher temperatures needed for their processing in the extruder, in comparison with the temperatures used in the internal mixer grafting, gave lower grafting degrees in the former process. Moreover, those processing conditions induced secondary reactions such as chain scission that lower the viscosity and stiffness of the functionalized material at the processing temperatures.

The chemical modification in the internal mixer of both SEBSs does not depend on the material viscosity at the processing conditions employed.

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