Viscoelastic and Morphological Study of Polyamide-6/Polyethylene/SEBS-g-DEM Ternary Blends

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ABSTRACT

The viscoelastic and morphological properties of ternary reactive blends of different low and linear low density polyethylenes, polyamide-6 and functionalized SEBS were studied. The SEBS was functionalized via reactive extrusion using diethylmaleate as the functionalizing monomer. Even though the grafting degree achieved was very low (about 0.040 wt%) due to the high melt viscosity of the SEBS, a lower particle size and no coalescence of the dispersed phase were obtained when SEBS-g-DEM was added to the blends and when the polyamide was the dispersed phase. There was no change in the dispersed phase size when the SEBS-g-DEM was used between 3 to 5%. However, when 10% was added, there was an increase in the volume average diameter due to the excess of emulsifier agent that builds up an additional dispersed phase. In addition to the viscosity ratio, the influence of the elasticity on the dispersed phase size is important and should be considered. When LLDPE and LDPE2 with similar viscosity curves were used as minor components, a finer dispersed phase was obtained with LLDPE which showed lower G' values.

INTRODUCTION

The development of new materials through immiscible polymer blending involves the incorporation of compatibilizing agents and/or the chemical modification of one of the blend components, in order to achieve some compatibility and to obtain a product with suitable properties. The incompatible character of blends of polyolefins with polar polymers brings about some problems due to their poor mechanical properties.

Chemical modification of synthetic polymers during processing offers new possibilities for improving original polymer properties. One important method for the compatibilization of immiscible blends is reactive blending. Compatibilization reduces the interfacial tension between the two phases and the physical size of the domains, stabilizes the morphology and enhances the interface adhesion [1].

Blends of polyethylenes and polyamide-6 are made in order to retain the most desirable properties of both components. However, a major drawback is related to the incompatibility of such blends that can be partially overcome by adding a suitable third component. Even though these blends have been studied exten-sively, their viscoelastic properties at low frequencies and high temperatures have not been reported yet. Hence, in this investigation, the viscoelastic and morpho-logical properties of ternary reactive blends of different polyethylenes, polyamide-6 and functionalized SEBS were studied.

EXPERIMENTAL

A polyamide-6 (PA1), two low density polyethylenes (LDPE), a linear low density polyethylene (LLDPE), and a SEBS thermoplastic elastomer (hydrogenated terpolymer of styrene/ethylene-butylene/styrene with a styrene content of 29%) were used. The characteristics of the polymers are reported in Table 1.

The grafting degree of SEBS was carried out in two stages in an intermeshing co-rotating twin screw extruder (Berstorff ECS2E25) at 238°C and 35 rpm. The functional monomer was diethylmaleate (DEM) and dicumyl peroxide (DCP) was used as initiator. At a first stage, a premix of 8 phr of DEM in SEBS was made, and at a second stage 0.5 phr of the initiator and 2 phr more of DEM were added. The functional monomer, as well as the peroxide, were added through the third feed port of the extruder due to the incomplete softening of the SEBS in the liquid feed port. Samples of the product were washed with o-dichlorobenzene (DCB) and methanol to eliminate the residual monomer, initiator and the DCB. Its

TABLE 1. Material Properties

Material	Density (kg/L)	$M_w \times 10^{-5}$	M_w/M_n	MFIx10³ (kg/10 min)	T_m ($\pm$ 1°C)
LLDPE	932	-	-	42	125
LDPE1	920	1.47	6.1	1.9-2.4	109
LDPE2	923	0.87	5.3	17-23	112
PA1	1130	-	-	-	220
PA2	1130	0.62	1.9	2.8[a]	219
SEBS 1652	910	Styrene block, M=7000 EB block, M =37500		styrene/rubber ratio 29/71	

[a] Determined at 230°C

grafting degree was determined by FTIR spectroscopy using a Nicolet Magna 750 spectrophotometer. The characteristic bands at 1736 and 1610 cm^{-1} were measured. A calibration curve made from absorbance ratios of those bands of mixtures of poly(diethyl fumarate) and SEBS was used following the method proposed by Fodor et al. [2].

Ternary blends of polyamide-6/polyethylene/SEBS (either unmodified or grafted) were prepared in an intermeshing co-rotating twin screw extruder (Werner & Pfleiderer ZSK 30) at 230°C and 180 rpm. The amount of SEBS-g-DEM in the blends was 3, 5 and 10 wt% of the total blend weight and the ratios polyamide-6/polyethylene were 80:20 and 20:80. The PA was dried before compounding in a vacuum oven for 16 hours at 85°C.

The apparent viscosities curves of the polymers were measured at 230°C as a function of apparent shear rate using a Capillary Rheometer Göttfert Rheograph 2000. A die with an L/D ratio of 20:1 and an entrance angle of 90° was used. The Bagley and Rabinowitch corrections were not made. Blends with the LLDPE and one of the LDPEs with similar viscosity were prepared at nominal shear rates where the viscosity ratio was close to unity, because the particle size that can be achieved should be the smallest [3]. The shear rate at every screw element was calculated following the method proposed by Michaeli et al. [4] and an average value at 180 rpm of 89 s^{-1} was used.

The viscoelastic properties of the homopolymers and their blends were measured in the linear viscoelastic range of strain using parallel plates in a Rheometrics Dynamic Analyzer (RDA-II) at 230°C. Strain sweeps were made at
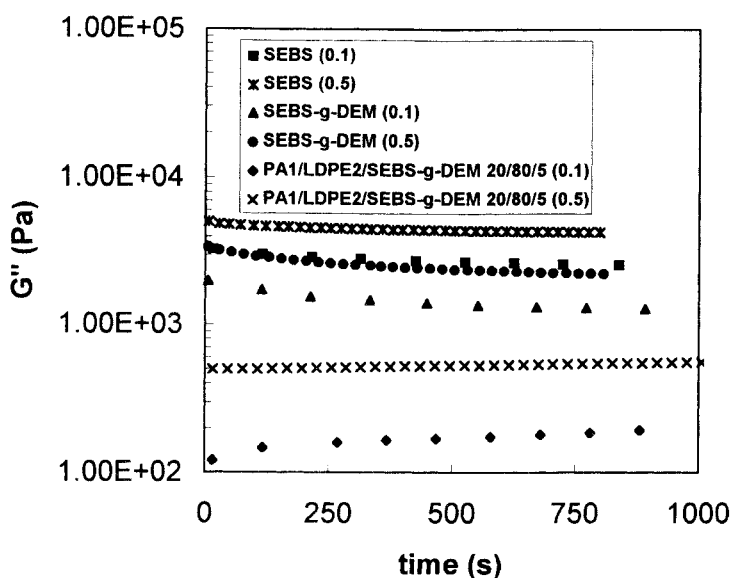
Figure 1.   Dynamic storage modulus (G') as a function of time at fixed frequencies of 0.1 and 0.5 rad/s at 230°C.

frequencies of 1 and 10 rad/s in order to fix the limits of that linear viscoelastic range. For the purpose of examining the thermal stability of the samples, time sweeps were performed at a fixed strain, 230°C and three different frequencies of 0.1, 0.5, and 1 rad/s because nitrogen atmosphere could not be employed. The frequency sweeps were conducted from 1 to 100 rad/s. Except for the lowest decade of frequency, all data points for each material were determined within a time span of t<5 min. The total time for loading, trimming and relaxing never exceeded 5 minutes.

Blend morphology was examined by SEM (Philips 505). Samples, both as extrusion strands and compression molded, were cryogenically fractured and covered with gold/platinum. The surface of few of the polyamide rich blends was etched using toluene.

RESULTS AND DISCUSSION

Linear viscoelastic behavior was seen at frequencies of 0.1, 0.5 and 1 rad/s in the strain range swept and up to a value between 10 and 20% of strain for frequencies higher than 1 rad/s up to 100 rad/s.
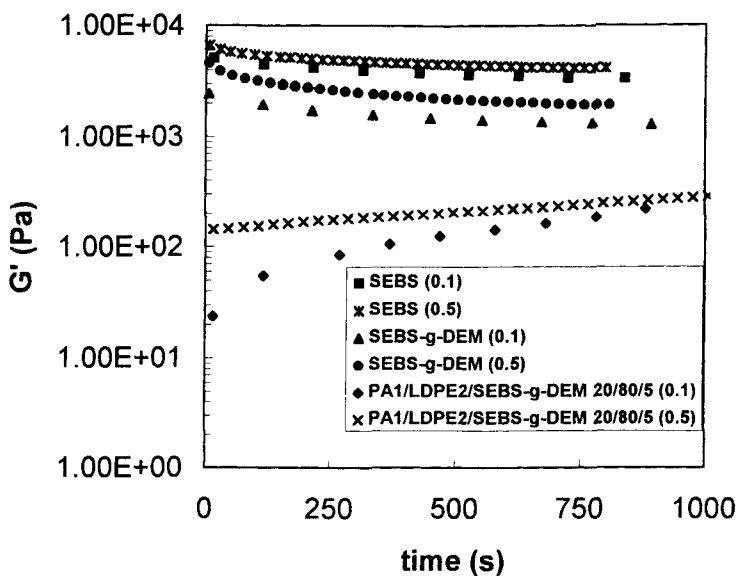
Figure 2. Loss modulus (G") as a function of time at fixed frequencies of 0.1 and 0.5 rad/s at 230°C.

Isothermal time scans were performed for up to 20 minutes at a fixed strain, at a temperature of 230°C and frequencies of 0.1, 0.5 and 1 rad/s. The results are illustrated in Figures 1 and 2, where the dynamic storage modulus (G') and the loss modulus (G") are plotted as a function of time (t). The thermooxidative degradation in air was observed to become noticeable at 0.1 and 0.5 rad/s, i. e., the error introduced by degradation on the viscoelastic properties was relatively important [5]. The SEBS underwent chain scission while chain extension was observed in the blends. At higher frequencies, no degradation was obtained. There-fore, the viscoelastic properties are reported from 1 rad/s. It is also noted that the storage modulus (G') is more sensitive than the loss modulus (G") to this type of degradation.

Figure 3 shows the dynamic viscosity data of the polymers as a function of frequency. It is seen there that the PA1 and the LLDPE show a Newtonian dynamic viscosity in the range 1 to 100 rad/s. On the other hand, the LDPEs and SEBSs show a shear thinning behavior. The SEBSs display higher viscosities in each frequency tested, the unmodified one showing the highest of all. The inflection in their curves is attributed to its elastomeric behavior.
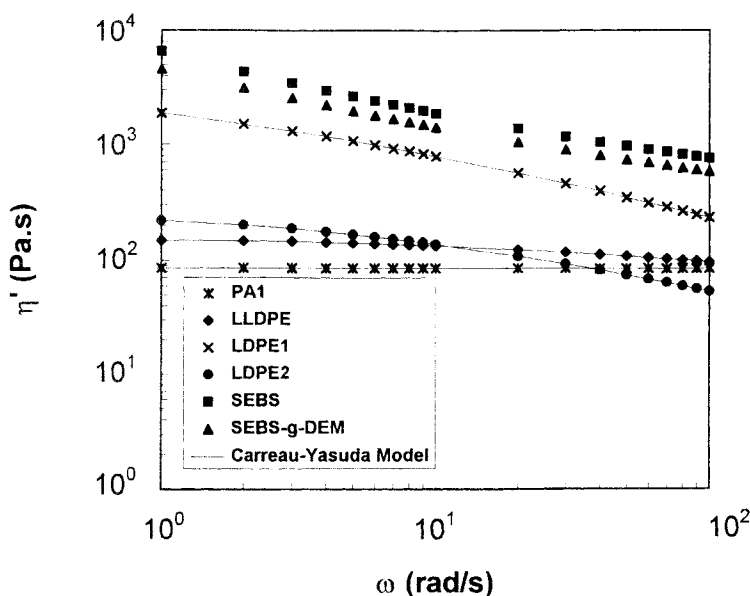
Figure 3.   Dynamic viscosity data (η') as a function of frequency of the polymers at 230°C.

A simple generalization of the Carreau-Yasuda model [6] was used to describe the dynamic viscosity as a function of frequency in the form:

$$\eta' = \eta_0 \ [1 + (\omega\tau)^\beta]^\alpha \tag{1}$$

where η_0 is the Newtonian viscosity, τ is the maximum relaxation time and α and β are equation parameters. For large deformation rates ($\omega\tau \gg 1$), a "power law" is recovered. The data of Figure 3 were fitted to Equation 1 in order to obtain the four constants listed in Table 2, which also show the power law constant K and exponent n from Capillary Rheometry of the polymers in the high shear rate range. The fit between experimental and theoretical curves was excellent (Figure 3), with a reduced standard error of measurements of less than 0.42%. All materials used have non-Newtonian characteristics at high shear rates, as indicated by the power law index n (n<1). Due to the plastic flow behavior of SEBSs, their viscosity curves did not fit the Carreau-Yasuda model.

The contribution of the viscous component to the viscoelastic behavior is given by the loss modulus (G") or the dynamic viscosity (η'), while the elastic behavior is represented by the storage modulus (G'). The plots log G' vs. log G"

TABLE 2. Carreau-Yasuda and Power Law Constants at 230°C

Material	η_0 (Pa.s)	τ (s)	α	β	$K \times 10^{-2}$ (Pa.s^n)	n
LLDPE	156.0	0.01152	0.6421	-0.6609	3.64	0.77
LDPE1	2214	1.1117	0.9512	-0.5358	28.7	0.58
LDPE2	229.4	0.1934	1.0999	-0.4296	8.99	0.58
PA1	86.3	0.00069	0.9555	-0.3651	1.46	0.89
SEBS					33.4	0.82
SEBS-g-DEM					13.3	0.86
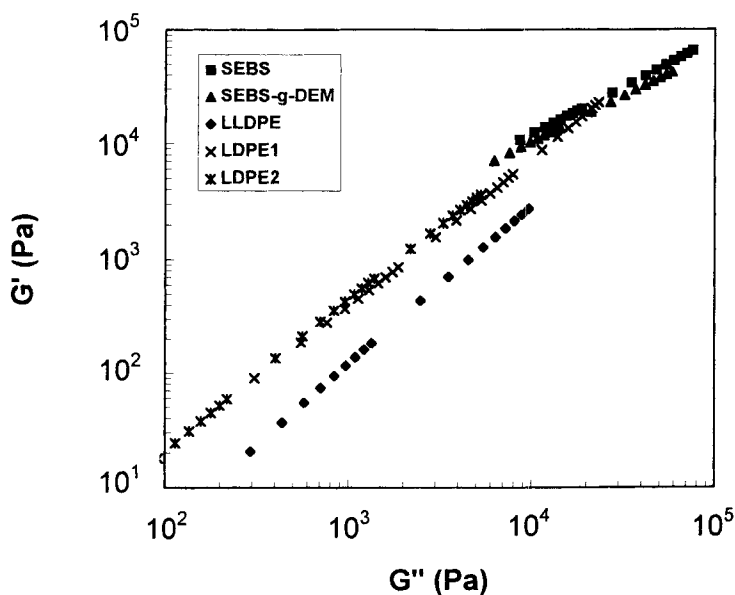
Figure 4.   G' as a function of G" at 230°C.

illustrate the relative contribution of the G' response to that of G" and are independent of molecular weight and temperature for homopolymers and miscible blends [7, 8]. Figure 4 shows that the SEBS behavior relates to its thermoplastic elastomer character (plastic flow behavior). As it can be seen in Figures 3 and 4, SEBS-g-DEM curves fell slightly below those of unmodified SEBS, which can be ascribed to the occurrence of chain scission during the functionalization process.

The average molecular weights of the LDPEs in Table 1 were calculated on the basis of the linear polyethylene calibration curve, without making any correction

TABLE 3. Influence of the Viscosity Ratio (VR) on the Particle Diameters and Viscoelastic Properties at Low Frequencies of the Extrudates

Blend	VR	D_n^b $\times 10^9$ (m)	D_v^c $\times 10^9$ (m)	η'^a $\times 10^{-3}$ (Pa·s)	G'^a (Pa)
PA1/LDPE1/SEBS-g-DEM (80/20/3)	4.3	5	8	-	-
PA1/LDPE1/SEBS-g-DEM (80/20/5)	4.3	5	7	0.08	32
PA1/LDPE1/SEBS-g-DEM (80/20/10)	4.3	2	11	0.13	63
PA1/LDPE1/SEBS-g-.DEM (20/80/5)	0.23	3	4	2.2	1290
PA1/LDPE2/SEBS (80/20/5)	1.3	3	11	-	-
PA1/LDPE2/SEBS (20/80/5)	0.77	5	14	2.5	1590
PA1/LDPE2/SEBS-g-DEM (80/20/5)	1.3	5	7	0.08	48
PA1/LDPE2/SEBS-g-DEM (20/80/5)	0.77	0.5	1	0.8	254
PA1/LLDPE/SEBS (80/20/5)	1.3	8	16	0.16	72
PA1/LLDPE/SEBS (20/80/5)	0.77	2	2	-	-
PA1/LLDPE/SEBS-g-DEM (80/20/5)	1.3	1	3	0.08	45
PA1/LLDPE/SEBS-g-DEM (20/80/5)	0.77	0.4	1	0.4	240

[a] Determined at 1 rad/s.

[b] Number-average particle diameter

[c] Volume-average particle diameter

for the presence of long-chain branching. Therefore, the corrected weight-average molecular weights, as well as the molecular weight distributions, could be higher. It has long been recognized that the degree of long-chain branching influences both the viscous and the elastic behavior of low density polyethylenes. The corrected number-average molecular weights are approximately the same for the LDPEs employed, but the corrected weight-average molecular weights vary from one another and materials with broader molecular weight distributions have lower viscosities and higher elasticity at high frequencies than polymers having narrow

TABLE 4. Particle Diameters of Molded Specimens and its Ratio Compared to Extrudates (DR)

Blend	DR[b]	D_n x 10^9 (m)	D_v x 10^9 (m)	D_v/D_n
PA1/LDPE1 (80/20)[a]	2.5	20	26	1.3
PA1/LDPE1 (20/80)[a]	1.5	12	20	1.7
PA1/LDPE1-g-DEM (80/20)[a]	1.3	5	8	1.6
PA1/LDPE1-g-DEM (20/80)[a]	1.5	3	3	1.0
PA1/LDPE2 (80/20)[a]	6.0	12	16	1.3
PA1/LDPE2 (20/80)[a]	4.0	16	33	2.1
PA1/LDPE2-g-DEM (80/20)[a]	2.0	6	6	1.0
PA1/LDPE2-g-DEM (20/80)[a]	1.0	2	2	1.0
PA1/LDPE2/SEBS (80/20/5)	3.3	10	16	1.6
PA1/LDPE2/SEBS-g-DEM (80/20/5)	4.0	4	8	2.0
PA1/LDPE2/SEBS-g-DEM (20/80/5)	1.5	0.6	0.8	1.3
PA2/SEBS (80/20)[a]	-	3	5	1.7
PA2/SEBS-g-DEM (80/20)[a]	-	0.7	1	1.4

[a] Perera *et al.* [9]
[b] DR=D_n of molded specimens/D_n of extruded specimens

molecular weight distributions due to the greater degree of chain entanglement that occurs in a broad distribution of molecular weight. This behavior can be seen in Figures 3 and 4 for the virgin materials.

Some morphological parameters of the blends and their viscoelastic properties at low frequencies are shown in Tables 3 and 4. It can be seen from Table 3 that even though the grafting degree achieved was very low (about 0.040 wt%) due to the high melt viscosity of SEBS, a lower particle size of the dispersed phase was obtained when SEBS-g-DEM was added to the blends and when the polyamide was the dispersed phase. Lower shear stresses are needed to deform and disperse the polyamide particles in the polyolefin matrix because of the lower shear viscosity and melt elasticity of the former.
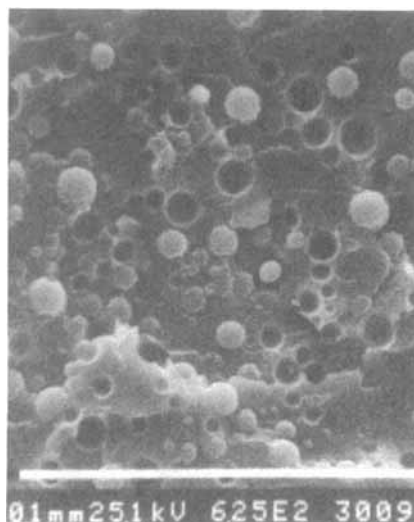
Figure 5.   SEM fracture surface of an extruded strand of PA1/LDPE1/SEBS-g-DEM 80/20/5 blend.

The influence of the amount of the compatibilizing agent on the particle size in polyamide rich blends is also shown in Table 3. There was no change in the dispersed phase size when the SEBS-g-DEM was used between 3 to 5%. However, when 10% was added, there was an increase in the volume average diameter (D_V) due to the excess of emulsifier agent that built up an additional dispersed phase. Table 4 shows that SEBS-g-DEM is more efficient lowering the particle size of the dispersed phase than grafted polyethylenes with higher grafting degrees [9]. The stability of the phases was examined by comparison of the dispersed domain size before and after compression molding of specimens. There was almost no change of the average particle diameter (i.e. no coalescence) after molding when SEBS-g-DEM was added to the blend (Table 4). Similar findings for reactive blends are reported in references 1 and 10.

Figures 5 to 10 show the SEM micrographs of the fracture surface of extruded strands of the blends. When Figures 5 and 6 are compared, it is seen that a cylindrical dispersed phase was obtained when the matrix was the high   melt viscosity LDPE1. In order to verify that the SEBS-g-DEM was located at the interface in polyamide rich blends, the fractured surface of some samples were etched in toluene. Figures 7 and 8 show that the compatibilizer indeed covered the PE dispersed phase. In Figures 9, 10 and 11, the effect of the grafting of the SEBS

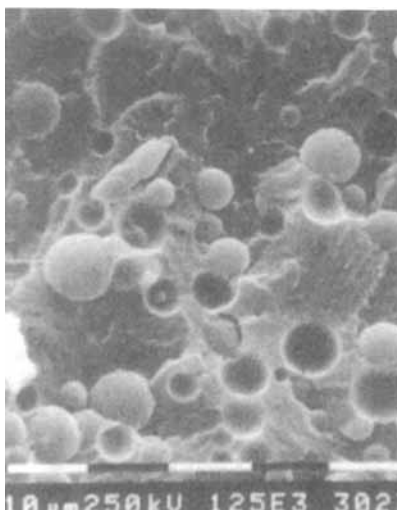**Figure 6.** SEM fracture surface of an extruded strand of PA1/LDPE1/SEBS-g-DEM 20/80/5 blend.

Figure 7. SEM fracture surface of an extruded strand of PA1/LDPE2/SEBS-g-DEM 80/20/5 blend.
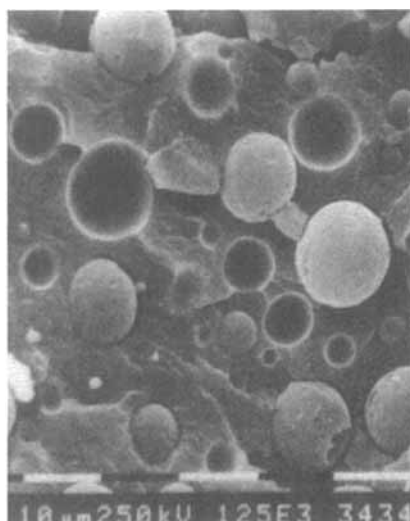
Figure 8.   SEM fracture surface of an extruded strand of PA1/LDPE2/SEBS-g -
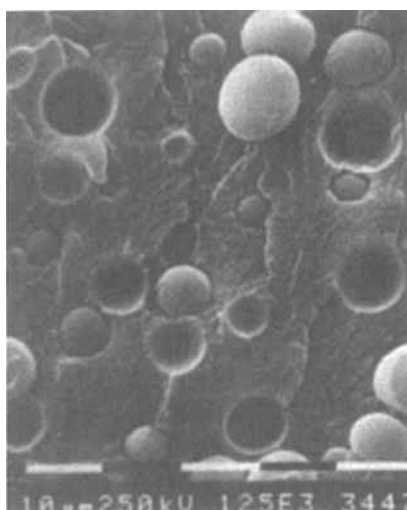DEM 80/20/5 blend etched with toluene

Figure 9.   SEM fracture surface of an extruded strand of PA1/LLDPE 80/20/5
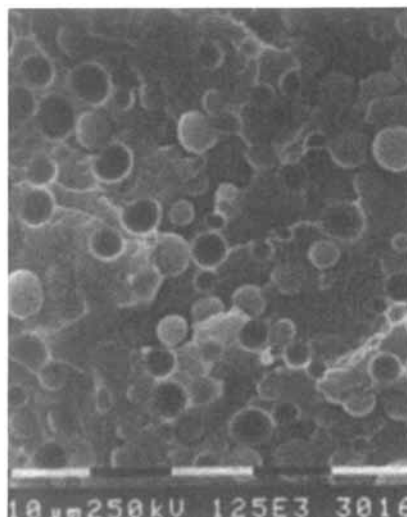blend.

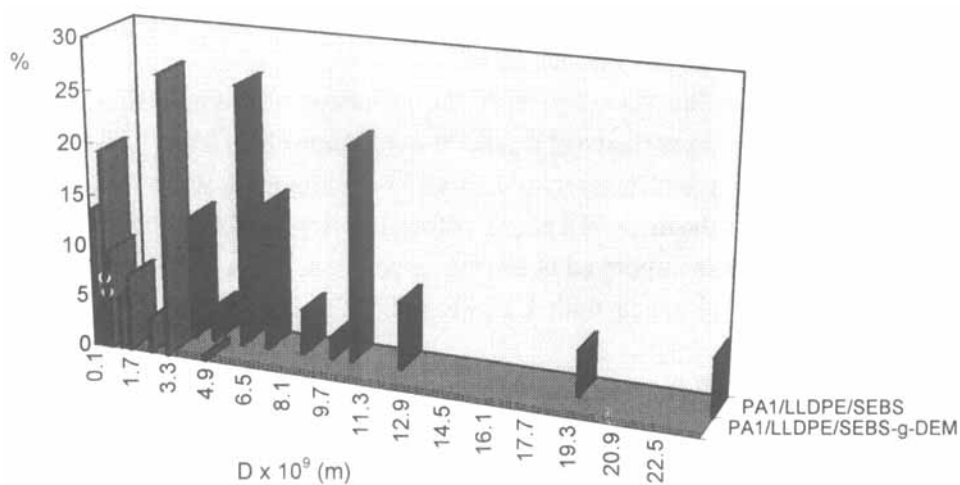**Figure 10.** SEM fracture surface of an extruded strand of PA1/LLDPE/SEBS-g-DEM 80/20/5 blend.

Figure 11. Histogram for the particle size distribution as percentage of number of particles vs particle diameter of PA1/LLDPE/SEBS and PA1/LLDPE/SEBS-g-DEM 80/20/5 blends.
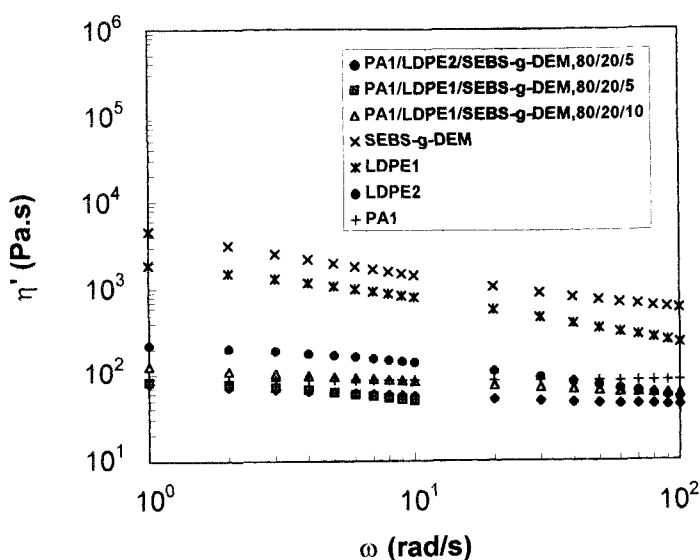
Figure 12. Dynamic viscosity (η') as a function of frequency of polymers and blends with a polyamide matrix at 230°C.

on the particle size can be seen. The larger dispersed phase particles disappear when SEBS-g-DEM was added to PA1 rich blends.

In addition to the viscosity ratio, the influence of the elasticity on the dispersed phase size is important and should be considered [11]. The viscoelasticity of the homopolymers at high temperatures is also very important when the material with a low G' value is the dispersed phase. When LLDPE and LDPE2 with similar viscosity curves were incorporated as the minor components in the blends, a finer dispersed phase was obtained with LLDPE (LLDPE showed lower G' values, Figures 7 and 10).

Figures 12 to 17 show the viscoelastic properties of the blends. As it can be seen in Figures 12 and 13, neither the particle size nor the polyethylene type or the SEBS-g-DEM modify the η' vs. ω and G' vs. G" curves when the polyamide is the matrix. As the SEBS-g-DEM covers the polyethylene particles, they become more rigid and elastic. The blend viscosities are lower than the individual polymer viscosities probably due to degradation during sample preparation [12], lack of proper drying [13] and/or to the presence of a cellular structure where very small particles of the PA are embedded inside the SEBS-g-DEM covered PE particles [14]. The same blends showed higher G' values when compared to the PA1 and
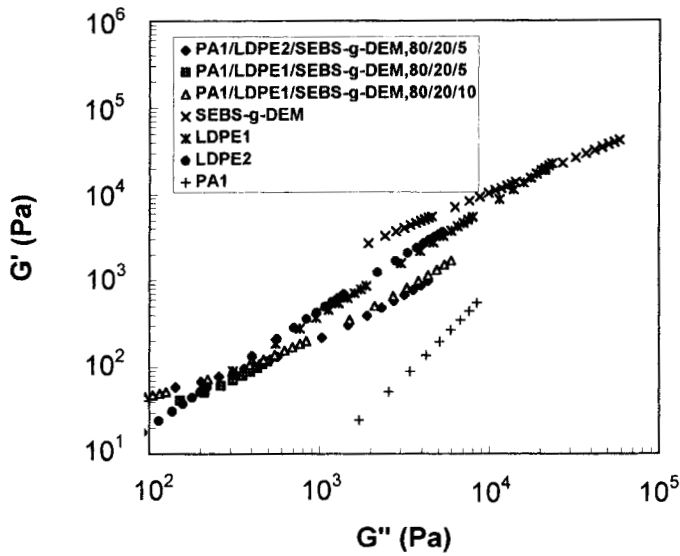
Figure 13. G' as a function of G" of materials in Figure 12 at 230°C.
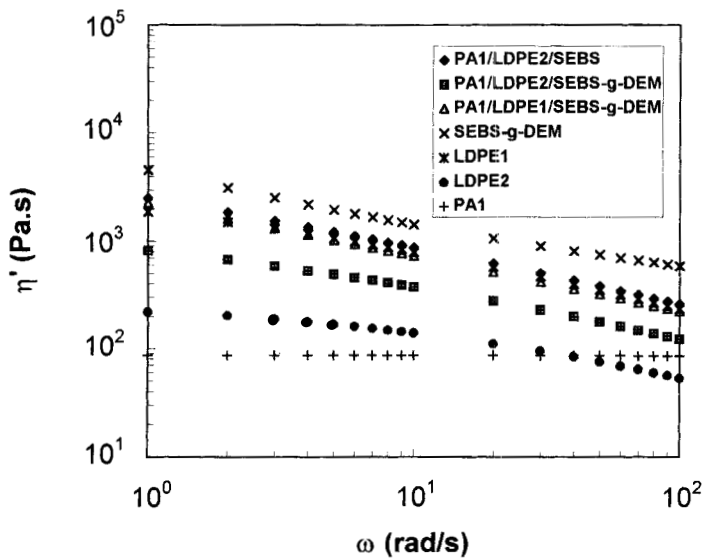
Figure 14. Dynamic viscosity (η') as a function of frequency of polymers and blends PA1/LDPE2/SEBS, PA1/LDPE2/SEBS-g-DEM and PA1/LDPE1/SEBS-g-DEM 20/80/5 at 230°C.
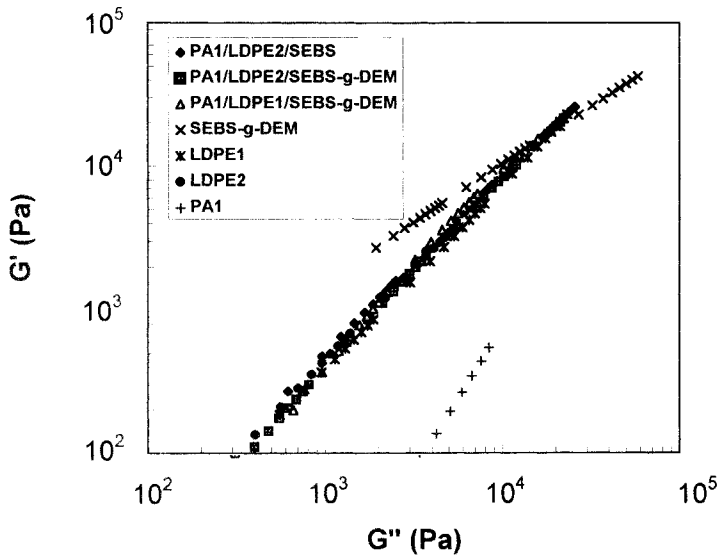
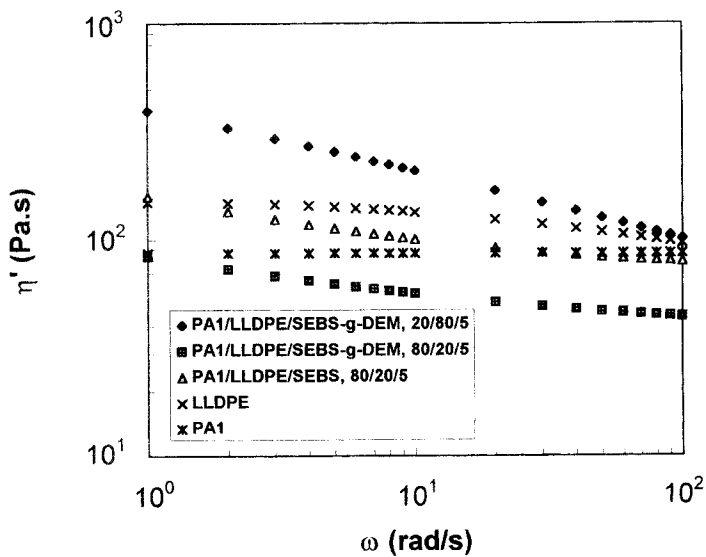**Figure 15.** G' as a function of G" of materials in Figure 14 at 230°C.

Figure 16. Dynamic viscosity (η') as a function of frequency of homopolymers PA1 and LLDPE and their blends at 230°C.
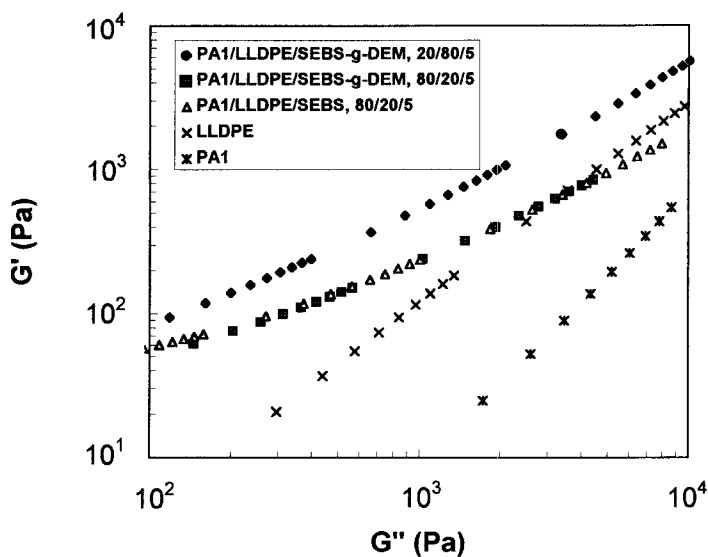
Figure 17.   G' as a function of G" of materials in Figure 16 at 230°C.

higher G' values at low frequencies when compared to polyolefins, due to the presence of the above mentioned small particles [15].

When the low density polyethylenes are the major components of the blends, their η' vs. frequency curves are dependent of the polyethylene type (Figure 14). Curves of blends with LDPE2 are located above those of the homo-polymers. A copolymer could have been formed (PE-SEBS-g-DEM-PA) and increased the viscosity. The curve of blend with unmodified SEBS is also located above those of its components and also above the curve of the same blend with SEBS-g-DEM. In that particular case, there are three different phases, one of which is very elastic and enhances the blend viscosity.

As Figure 15 shows, G' vs. G" curves of 20/80/5 blends of PA1/LDPEs/SEBS either grafted or not, are independent of the type of homopolymer. These blends are much more elastic than the polyamide.

Figures 16 and 17 show figure η' vs. frequency and G' vs. G" of compatibilized blends of PA1 with LLDPE and modified and unmodified SEBS. When the dispersed phase is the PA, the viscosity curve of the blend is located above the viscosity curves of its components. On the other hand, the blend where the dispersed phase is the LLDPE and SEBS-g-DEM is used has a viscosity curve that falls below the same blend with unmodified SEBS. From the elasticity point

of view, blends of PA1/LLDPE and SEBS both grafted or not, have a higher elastic modulus than their individual components do.

CONCLUSION

Even though the grafting degree achieved was very low (about 0.040 wt%) due to the high melt viscosity of the SEBS, a lower particle size and no coalescence of the dispersed phase were obtained when SEBS-g-DEM was added to the blends and when the polyamide was the dispersed phase. There was no change in the dispersed phase size when the SEBS-g-DEM was used between 3 to 5%. However, when 10% was added, there was an increase in the volume average diameter due to the excess of emulsifier agent that builds up an additional dispersed phase. In addition to the viscosity ratio, the influence of the elasticity on the dispersed phase size is important and should be considered. When LLDPE and LDPE2 with similar viscosity curves were used as the minor components, a finer dispersed phase was obtained with LLDPE which showed lower G' values.

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