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Effects of processing parameters on the properties of microwave-devulcanized ground tire rubber/polyethylene dynamically revulcanized blends

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ABSTRACT: This work aimed to evaluate the effects of processing parameters on properties of dynamically revulcanized blends based on 60 wt % of devulcanized ground tire rubber (GTR) and 40 wt % of high density polyethylene (HDPE). Devulcanization of the GTR was carried out in a system comprised of a conventional microwave oven adapted with a motorized stirring system with speed control. The resulting devulcanized GTR contained 26 wt % soluble in toluene. It was processed with HDPE in a twin screw extruder to produce a dynamically revulcanized blend. Processing parameters such as screw speed and feeding mode were varied. Their effects were evaluated based on tensile, dynamic mechanical, thermal and rheological properties, as well as on morphology. The results show the importance of the processing parameters involved in the production of blends with dynamically revulcanized rubber phase in the extruder, and good match between the residence time of the rubber and its revulcanization kinetics. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43503.

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INTRODUCTION

A thermoplastic vulcanizate (TPV) is a thermoplastic elastomer (TPE) produced by dynamic vulcanization of an elastomeric phase in a thermoplastic matrix.[1–3] Morphologically, such a blend is described as a dispersion of small particles of a vulcanized elastomer in a thermoplastic matrix,[4] where the matrix phase acts as a sort of glue. This type of blend has a typical elastomeric mechanical behavior at room temperature while being able to be processed like a thermoplastic in the molten state.

Devulcanization of waste rubber aims at restoring the flow capacity of the vulcanized rubber by breaking-up its cross-linkings. Devulcanization provides moldability to the rubber, decreasing the viscosity of the thermoplastic/recycled rubber blends, favoring their processability and improving its properties. In a very recent work, de Sousa *et al.*[5] proved that the devulcanization of ground tire rubber (GTR) by microwaves increased its fluidity during processing of the blends of GTR devulcanized by microwaves and high density polyethylene (HDPE) in an internal mixer. Correspondingly, Garcia *et al.*[6] studied physical and chemical changes occurred in the GTR after microwaves exposure, and proved that the treatment promoted the breaking of sulfur cross-linkings and consequently increased the rubber fluidity. In addition, de Sousa and Scuracchio[7] highlighted that the temperature increase is responsible for devulcanization, which depended both on the amount of carbon black present in the rubber and the time of exposure to microwaves. Using another approach, Seghar *et al.*[8] used an ionic liquid for styrene-butadiene rubber (SBR) in order to enhance the absorption of the microwaves energy during the treatment. They found an energy absorption threshold of 220 Wh/kg above which the cross-linkings density starts to significantly decrease.

The morphology of blends depends on thermo-mechanical conditions they are subjected to. Factors affecting these conditions include: material properties (viscosity and elasticity ratios between polymer components, interfacial tension), compositions of the polymer components, mixer's characteristics (type and dimensions), and operating conditions (temperature, screw speed and feed rate in the case of a twin screw extruder).[9–13] The morphology of TPV blends is dictated by the balance between break-up and coalescence of the elastomer phase droplets during processing. In the special case of blends containing a devulcanized elastomer phase, devulcanization promotes the break-up, while the revulcanization reduces coalescence. Both phenomena promote a finer morphology.[5]

Some works reported the effects of processing parameters on the properties of TPVs.[14–17] Others described the use of recycled rubbers and thermoplastics for the production of this type of blend as an important way to value recycled materials.[18–36]

Kalkornsurapranee *et al.*[37] analyzed the influence of mixing parameters in the production of TPVs natural rubber (NR)/thermoplastic polyurethane (TPU) in an internal mixer on its mechanical properties. The speed of the rotors influenced directly the final morphology of blends and its tensile strength. However, as observed by other authors,[38] there are optimum processing conditions, which may vary according to the system analyzed. For example, the most appropriate shear rate is not necessarily the highest one. A high shear rate may bring about thermomechanical degradation of NR. On the other hand, a low shear rate may produce blends with poor mechanical properties due to insufficient reduction of NR particle size and distribution in the TPU matrix. Joubert *et al.*[39] performed a work with similar purposes through the production of TPV copolymer of ethylene and vinyl acetate (EVA)/polypropylene (PP), and its properties were strongly dependent on the morphology, and consequently on the process. For the blends produced at lower shear rates, the morphology was composed of geometrically well-defined individual EVA particles, while for the ones produced at higher shear rates, shapes of EVA particles were not well defined. Kim *et al.*[40] studied the effects of the screw configuration on mechanical properties and morphology of maleic anhydride grafted polypropylene/GTR. Xin *et al.*[41] analyzed the influence of processing parameters on the foamed blends of GTR/PP by using a single screw extruder and statistical analysis. It turned out that the screw speed was the most important parameter which determined the cell size and cell density. In short, the influences of different processing parameters on mechanical properties are associated with their influences on morphology.[42]

In this work, a twin screw extruder is used to prepare dynamically revulcanized blends based on devulcanized GTR and HDPE. The effects of processing parameters such as screw speed and number of feeders (feeding mode) on shear stress/rate and residence time is emphasized, which may affect the cross-linking density of the rubber phase, as well as its domain size in the matrix and, consequently, properties of the resulting blend. Properties evaluated in this work are tensile, dynamic mechanical, thermal and rheological. The ultimate goal of this work is to develop a route to prepare a typical TPV blend.

EXPERIMENTAL

Materials

The HDPE used was a commercial product of Braskem (Melt Flow Rate, MFR (190 °C/2.16 kg) = 7.3 g/10 min) with the trade name IA-59. The GTR was ground waste truck tire separated from nonelastomeric components. It had a volumetric mass of 1.17 g/cm^3, particle sizes ranging from 297 to 37 µm (according to ASTM D5644-01) and sol fraction of 12.2% (according to ASTM 2765-11, using toluene as a solvent). The composition of the GTR was unknown but it is known that it usually contains polyisoprene (NR), SBR and/or polybutadiene (BR),[43–45] as well as additives such as vulcanizing agents, softeners and fillers.[6] The GTR, rubber accelerator TBBS (N-tert-Butyl-2-benzothiazole sulfenamide) and sulfur were kindly supplied by Pirelli.

Devulcanization of the GTR and Mixing with Vulcanizing Agents

The GTR was devulcanized in a system comprised of a conventional microwave oven adapted with a motorized stirring system with speed control. The whole devulcanization process was done using the maximum power of the oven at 820W. The time at which the material was exposed to the microwaves was 5.5 min, the optimum devulcanization time for the process under investigation. The resulting material was designated as GTR5.5. Its sol fraction in toluene was ∼26% (according to ASTM 2765-11).

According to the thermogravimetric analysis in the literature,[43] GTR undergoes two decomposition stages between 300 and 500 °C under nitrogen atmosphere. The first one corresponds to the NR, and the second to the SBR. Considering the highest temperature of the GTR5.5 during the microwaves treatment, the devulcanization and degradation occurred mainly in the NR phase.[44] Thus it can be assumed that the main component of the GTR5.5 was SBR.

The GTR5.5 was mixed with the vulcanizing agents by using a laboratory two roll mill PRENMAR for approximately 6 minutes at room temperature. To promote the dynamic revulcanization, 1 phr of the accelerator N-tert-butyl-2-benzothiazole sulfenamide (TBBS) and 1 phr of sulfur were added to the mixture.[24] The concentrations of the additives were optimized in order to simplify the dynamic revulcanization process and to facilitate further analyses.

Rheological Measurements of the Devulcanized GTR

The revulcanization characteristics of the GTR5.5 were studied by using a Rubber Process Analyzer (RPA) Tech Pro, model Rheo Tech MDPT, according to ASTM D1646-07. Curves of torque versus time were obtained at 180 °C. The rheological properties such as scorch time (ts_1, the time necessary for torque to reach 1,3 x 10^{-6} N m above the minimum torque) and optimum cure time (t_{90}, the time for torque to reach 90% of the maximum torque) were obtained from the curves.

Preparation of the Blends and Analysis of the Best Processing Conditions

Blends were prepared in a twin-screw extruder of type Process 11 Thermo Scientific with 2 different feeding modes (Figure 1). The temperatures of the barrel zones were fixed at 180 °C, except the third zone for the second feeding mode [Figure 1(b)] whose temperature was fixed at 120 °C to facilitate the introduction of the rubber phase. The effects of screw speed and feeding mode were studied with blends composed of 40 wt % of HDPE

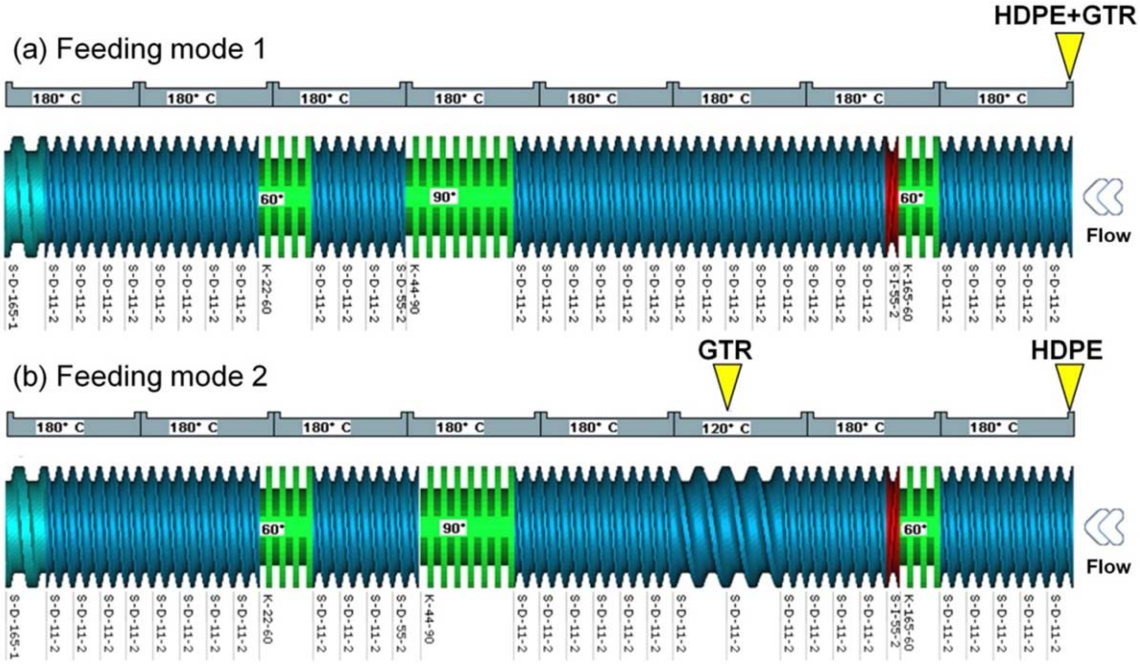

Figure 1. Two different feeding modes used for the preparation of the blends: (a) Feeding mode 1: both HDPE and GTR5.5 were added in the same feeder; (b) feeding mode 2: the HDPE was added in the first feeder and the GTR5.5 in the second one. The screw channel in the region of the second feeder was deeper and wider to facilitate the GTR5.5 feeding. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and 60 wt % of GTR5.5. The screw speed was 100, 150, 200, 250, and 300 rpm, respectively. The blends produced in the extruder through feeding mode 1 were denoted by the corresponding screw speed in rpm, and those produced through feeding mode 2 were designated as the corresponding screw speed in rpm followed by 2.

The materials were taken directly from the extruder die and were injected using a micro injection molding machine 12cc Explore. The temperature of the injection unit was 180 °C and that of the mold was 45 °C. The material inside the mold was maintained at 15 bars for 10 s. The mold dimensions were based on ASTM D 412 type A.

Characterization

The tensile properties of the blends were evaluated by using a dynamometer MTS Systems Qtest 150 Elite. The rate of grip separation was 50 mm/min.

A Jeol JSM-6490LJ Scanning Electron Microscope (SEM) was used to characterize the morphology of the blends. The injected molded samples for the tensile testing were fractured in liquid nitrogen and the GTR phase was selectively extracted by cyclohexane at 70 °C for 12 min. The samples were dried in a vacuum oven at 100 °C for 30 min and then coated with a mixture of gold and palladium by using a sputter coater. Scuracchio *et al.*[46] selectively extracted the SBR phase of the SBR/polystyrene (PS) blends by using a solution containing 10 mL of H_2SO_4, 30 mL of H_3PO_4, 30 mL of water, and 5 g of CrO_3 at 70 °C for 5 min. That extraction procedure was also performed on the blends. The diameters obtained by the SEM images were close to those obtained by extraction in cyclohexane.

Different micrographs were taken for each blend and were analyzed by the image analyzer software ImageJ to determine the diameter of each particle. At least 100 particles of each blend were analyzed. The number average diameter (D_n) and the volume average diameter (D_v) were calculated according to Chen *et al.*[47] More information about the mentioned method can be found in the work of Mani *et al.*[48]

Dynamic mechanical properties of the blends as function of temperature were analyzed by a Dynamic Mechanical Analyzer (DMA) of type DMA Q800 TA Instruments. The analyses were performed under the following conditions: single cantilever mode, frequency of 1 Hz, temperature range from −100 to 140 °C and heating rate of 3 °C/min. The dimensions of the samples were ~17.5x12.5x2 mm.

Rheological properties of the blends were analyzed by oscillatory rheometry in a parallel plate rheometer Anton Paar CTD450 (diameter 25 mm, gap 1.3 mm, 1% of strain at 180 °C). Frequency sweep experiments were carried out in the linear viscoelastic range to characterize the viscoelastic properties of the blends. The frequency ranged from 0.1 to 100 rad/s and prestrain sweep tests were performed to determine the linear viscoelastic range of the blends.

Thermal properties of the HDPE phase were analyzed by a Differential Scanning Calorimeter (DSC) of type DP Union DSC Q200 under nitrogen atmosphere. The samples were heated from room temperature to 190 °C and were held at this temperature for 3 min to erase their thermal history and melt the HDPE. They were then cooled to −50 °C and were subsequently heated to 200 °C. All the steps were performed at 10 °C/min.

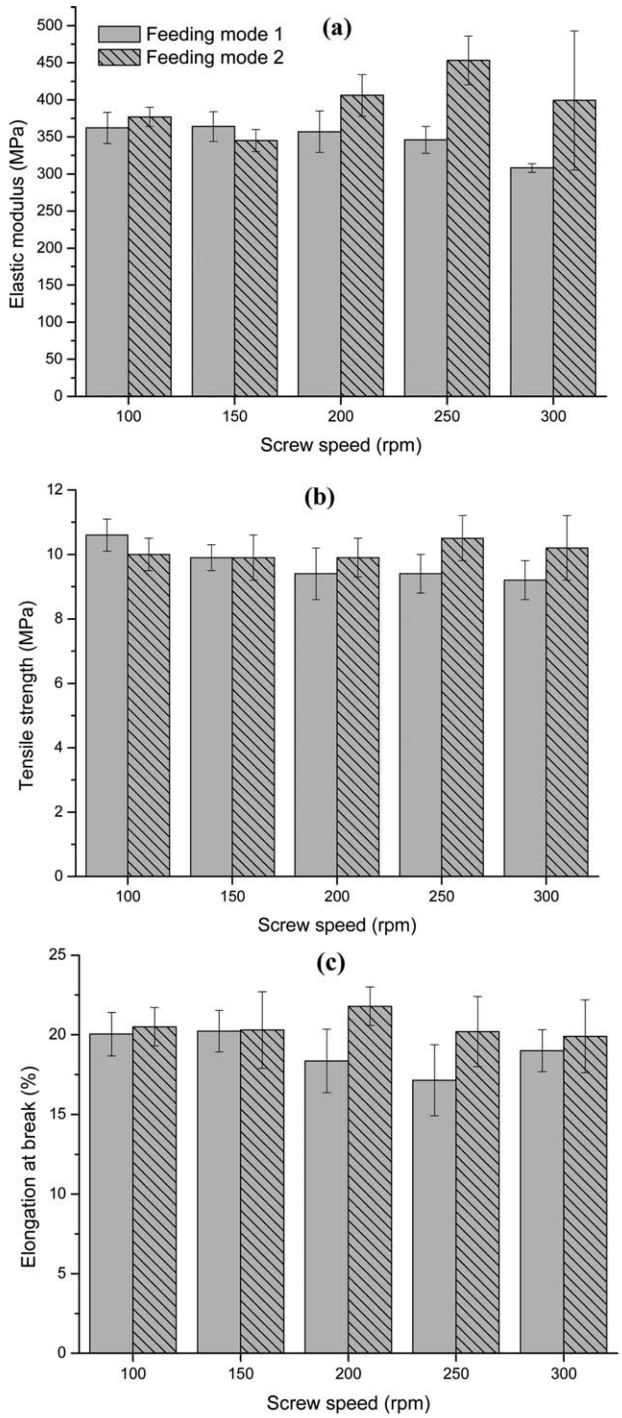

Figure 2. Tensile properties of the blends produced through feeding modes 1 and 2: (a) elastic modulus, (b) tensile strength and (c) elongation at break.

RESULTS AND DISCUSSION

According to the rheological measurements of the GTR5.5 with the vulcanizing agents (TBBS and sulfur), the values of ts_1 and t_{90} were 27.0 and 43.8 s, respectively.

In what follows, the results of the blends obtained through feeding mode 1 will be compared with those through feeding mode 2 in terms of morphology, tensile, dynamic mechanical, oscillatory rheological, and thermal properties.

Tensile Properties

Figure 2 compares the tensile properties of the blends between feeding modes 1 and 2. Overall, the effects of screw speed on the mechanical properties are not significant. Moreover, the mechanical properties of the blends are far below those of classical TPVs, probably because of the poor compatibility and adhesion between GTR5.5 and HDPE.

Mahallati and Rodrigue[49] observed the influence of feeding strategy on the mechanical properties of blends of PP/recycled ethylene-propylene-diene monomer (r-EPDM). According to them, the location of the second feeder needed to be optimized to reach a good balance between dispersion and rubber particle treatment. They found better mechanical properties when the r-EPDM was separately introduced in the first feeder due to better interaction between the phases. As a conclusion, feeding sequence had a strong influence on the properties of the blends due to the dependence of the properties on the mixing quality during processing.

On the other hand, properties of a TPV composed of a recycled material depend on the concentration of the regrind, as well as on the adhesion between the polymer phases.[26] When the compatibility or adhesion between the phases is poor, whatever the processing parameters, their influences on the mechanical properties of the blends may not be large. However, in this work the tensile properties of the blends produced through feeding mode 2 slightly outperform those through feeding mode 1, especially elastic modulus. This is probably due to differences in morphologies, as will be shown later.

In an earlier study,[5] revulcanized blends composed of devulcanized GTR/HDPE were produced in an internal mixer, and the exposure time of the GTR was varied. As observed in the present work, the mechanical properties were far from typical TPV due to the lack of adhesion between the phases. Adding a nanometer scale filler to the system[50] did not make much difference. However, the properties of the blends produced in the extruder in this work are much better than those produced in the internal mixer, due to better dispersion of the GTR in the matrix.

According to Lee *et al.*,[20] it is not easy to produce polymer blends composed of a thermoplastic and GTR due to the lack of thermodynamic compatibility between them. The latter can be improved through surface treatment of the rubber and dynamic vulcanization of the elastomer phase. The devulcanization of the elastomer phase by microwaves improves the compatibility between the phases of the blend. However, according to Kumar *et al.*,[51] the prerequisites of manufacturing blends containing GTR are: use of an additional (fresh) elastomer and/or devulcanization of the GTR at least partially, what is performed on the present work in order to increase the compatibility between the phases. Even performing devulcanization of the GTR phase, both the lack of compatibility and adhesion between the phases contributed to the deterioration of the mechanical properties of the blends, no matter the processing parameters adopted.

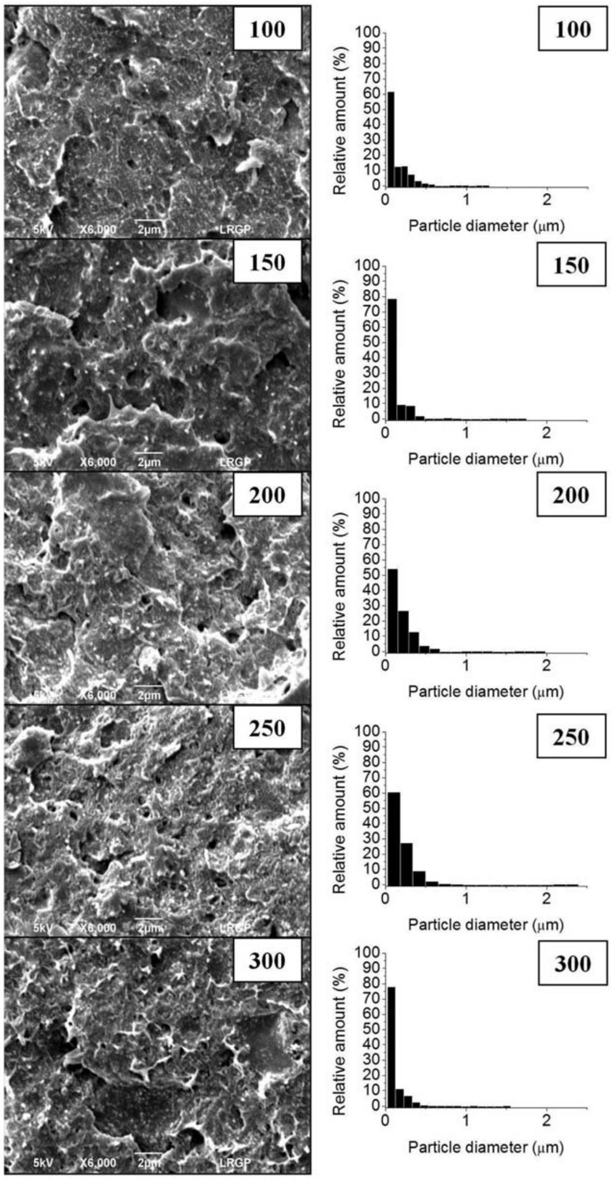

Figure 3. SEM images of the blends produced through feeding mode 1 for 5 different screw speeds and their particle size distributions.

Morphology

Figures 3 and 4 show the SEM images of all the blends produced through the two different feeding modes and their particle size distributions. The black areas correspond to GTR5.5 particles selectively extracted by cyclohexane.

First of all, it is seen that devulcanized GTR particles are all finely dispersed in the HDPE after the extrusion step in the twin screw extruder. Moreover, the higher the screw speed, the finer the rubber particles, and the narrower the particle size distribution. The rubber particles are smaller in size for the blends obtained by feeding mode 2 (Figure 4). This is probably due to a higher shear stress/rate imposed to the rubber particles, or due to the absence of premature revulcanization of the rubber phase. This tendency was also observed by Yquel *et al.*[52] and George *et al.*[16] The latter prepared nitrile rubber (NBR)/HDPE TPVs under different processing conditions in terms of barrel temperature, screw speed, among other factors. They found that the size of the rubber particles decreased with increasing the screw speed.

Table I summarizes the morphological parameters from the SEM images of the GTR5.5/HDPE blends in terms of the number average particle size (D_n), volume average particle size (D_v), and size dispersion (D_v/D_n). It is noted that the effects of the feeding mode and screw speed on the rubber domain size and the particle size distribution are not obvious. Nevertheless, the blend 250-2 presents the smallest size, the narrowest particle size distribution and the highest elastic modulus. The “best result” is a consequence of an optimum trade-off between the dispersion and revulcanization of the devulcanized GTR in the extruder.

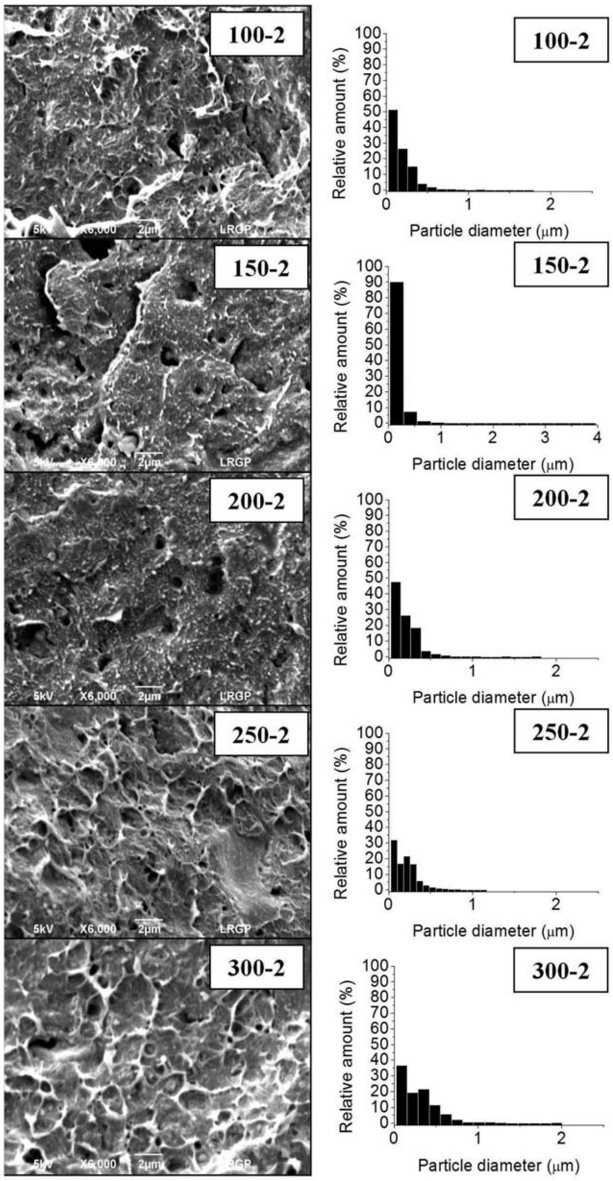

Figure 4. SEM images of the blends produced through feeding mode 2 for 5 different screw speeds and their particle size distributions.

Table I. Morphological Parameters of the Blends

Feeding mode 1				Feeding mode 2			
Sample	D_n (μm)	D_v (μm)	D_v/D_n	Sample	D_n (μm)	D_v (μm)	D_v/D_n
100	0.14	0.65	4.59	100-2	0.18	0.71	3.87
150	0.14	1.33	9.84	150-2	0.20	2.65	13.41
200	0.19	1.16	6.04	200-2	0.20	0.96	4.82
250	0.19	1.30	6.68	250-2	0.20	0.58	2.89
300	0.12	0.75	6.46	300-2	0.30	1.04	3.52

One of the most important factors that influence the morphology of a polymer blend is the viscosity ratio, *p*, defined as follows:

$$p=\frac{\eta_d}{\eta_m} \tag{1}$$

where η_d and η_m are the viscosities of the disperse phase and the matrix, respectively, at the same conditions of temperature and shear rate. It is generally accepted that a viscosity ratio close to 1 generates the smallest particle size in a purely shear flow.[53] However, other characteristics like elasticity of both phases and the complexity of the flow have to be taken into account.[54] In our system, the rheological properties of the disperse phase change dramatically along the process, as a result of dynamic revulcanization and the complicity of the flow field typical of twin screw extrusion. It is impossible for this work to provide a quantitative analysis of the change in viscosity ratio. Nevertheless, it is expected that the viscosity ratio increases with increasing dynamic revulcanization. The final morphology of this type of blend is also highly dependent on the rheology of the elastomeric phase along the processing. The good knowledge, prior analysis, and adequacy of the process parameters with the rheological properties of the rubber will help to reach a more refined morphology and satisfactory mechanical properties. Based on the results of their studies, Kalkornsurapranee *et al.*[37] concluded that the optimization of the processing parameters is a key factor in the control of the TPV properties.

Figure 5 shows some vulcanization parameters involved in the processing of dynamically revulcanized blends, as well as the scheme of a probable evolution of morphology during processing. The screw profile is for feeding mode 2, since it produced finer morphology. Figure 5 shows that at point 1 of the extruder, there is only physical mixing between the phases and there is no revulcanization of the GTR5.5. At the beginning of the second high shear zone, the revulcanization reaction starts (the residence time of the rubber from its introduction in the extruder to this point is about the same of ts_1 of the reaction) and, around point 2, the blend presents a co-continuous morphology in which the elastomeric phase is stretched in the flow direction.

At this stage, the overall viscosity is increased [as well as the *p* value—eq. (1)], and the elastomeric phase with high elasticity is stretched and breaks into smaller particles due to high shear rates, intense elongational flow and high elasticity generated by cross-linkings (point 3), resulting in high mechanical stresses. At point 4, still under the effect of high shear rates, rubber particles break into smaller particles, and at point 5 there is a better distribution in the thermoplastic matrix. The end of the second shear zone (point 4) refers approximately to the optimum cure time of the elastomeric phase which, in the case of GTR5.5, is 44 s. The residence time of rubber from its introduction in the extruder to the end point of the reaction must be equivalent to t_{90}, and this point should be in a high shear zone of the extruder for breakage of rubber particles in micrometric dimensions.

It is important to address here that, for both screw profiles used, the first mixing zone served to melt the HDPE, the second one to dynamically revulcanize the GTR phase and the last one to improve the distribution of the rubber particles in the HDPE. In the case of the blends produced through feeding mode 1 [Figure 1(a)], the high shear rate in the first mixing zone could bring about premature revulcanization of the rubber phase, since the components were added together. As the length of this zone and the corresponding residence time were short, the time for the reaction to go to completion was longer than the residence time on the zone, which probably happened in the second transport zone. Thus, the rubber domains were not sufficiently well dispersed and distributed in the HDPE matrix. However, in the case of the blends produced through feeding mode 2 [Figure 1(b)], the residence time of the rubber phase inside the extruder from its introduction to the end of the second mixing zone was closer to the optimum cure time of the GTR5.5 at 180 °C (43.8 s). Therefore, the mixing zone was long enough for the revulcanization reaction to go to completion and the dispersed rubber domains to have its size reduced in the HDPE matrix.

The blend 250-2 presented much finer morphology and consequently better mechanical properties, despite the fact that the compatibility and adhesion between the phases were poor. The finer morphology is due to good match between processing conditions and rheological properties of the GTR5.5. The residence times of the GTR5.5 inside the extruder from its introduction to the respective points shown in the Figure 5 were ~50 and 30 s, respectively, which were very close to the values of t_{90} and ts_1 (44 and 27 s, respectively).

The above analyses show that processing parameters are very important for controlling the morphology and consequently the mechanical properties of the blends. In what follows, the influences of those parameters will be discussed in terms of dynamic

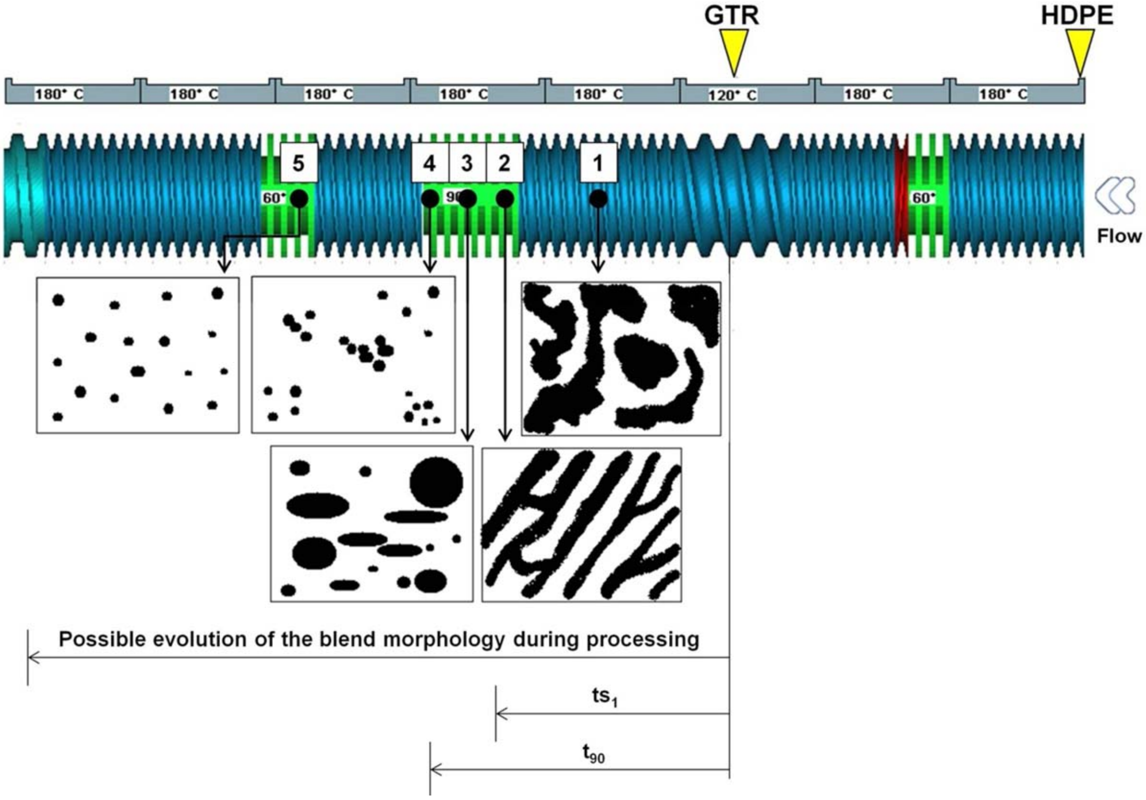

Figure 5. Screw profile relative to Figure 1b (feeding mode 2) used in the preparation of the blends, showing the schema of the possible evolution of the morphology and rheology of the elastomeric phase involved during processing. In the images that represent the morphologies, the black part represents the elastomeric phase and the white represents the thermoplastic phase. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mechanical, oscillatory rheological, and thermal properties of the blends.

Dynamic Mechanical Properties

Figure 6 shows the storage modulus (E') and tan δ of the blends produced through the two feeding modes as function of temperature. The initial decrease of E' [Figure 6(a,b)], at low temperatures (between −50 and 0 °C), is related to the glass transition temperature (T_g) of the elastomeric phase. In general, the values of E' at low temperatures of the blends produced through feeding mode 1 are higher than those produced through feeding mode 2, due to higher cross-linking densities[22,55] as a result of a longer screw length (residence time) for the revulcanization. This is further confirmed by oscillatory rheometry data. As both phases were added together, the residence time of the elastomeric phase was high enough to increase the cross-linking density of the GTR phase of those blends. In other words, the residence time of the elastomeric phase during processing was responsible for its cross-linking density in the blend.

Regarding the results of tan δ [Figure 6(c,d)], all blends show two peaks, one at temperatures from −35 to −30 °C and the other one from 65 to 130 °C. The first peak refers to T_g of the elastomeric phase, while the second one refers to the α transition of the thermoplastic phase (T_α). The temperature at which α transition occurs is influenced by the average thickness of the crystallites. According to Jose *et al.*,[28] the increase in the peak intensity implies increased chain mobility of the HDPE phase and hence improved toughness of the HDPE phase. However, further studies are required to understand this observation.

By observing the data obtained in DSC, it is clear that the presence of the rubber has a strong influence on the crystallization behavior of the HDPE, due to nucleating effects. Not only does the amount of the crystalline phase change, but also the morphology of the crystals are influenced by the presence of the disperse phase. This will be discussed in more detail in the corresponding section.

The values of the glass transition of the elastomeric phase of the blends were obtained according to the values of the maximum peaks in Figure 6(c,d). They ranged from −34 to −35 °C. Hence, no significant changes were observed among the different materials.

Oscillatory Rheological Properties

Figure 7 shows the storage modulus (G') and complex viscosity (η^*) as a function of the frequency of the blends produced through feeding modes 1 and 2. It is seen that the complex viscosity of the blends decreased with increasing frequency. This is a typical shear thinning behavior, according to the Cox-Merz rule.[56–60] Moreover, the values of G' and η^* of the blends produced through feeding mode 1 were higher than those of the blends produced through feeding mode 2 because the

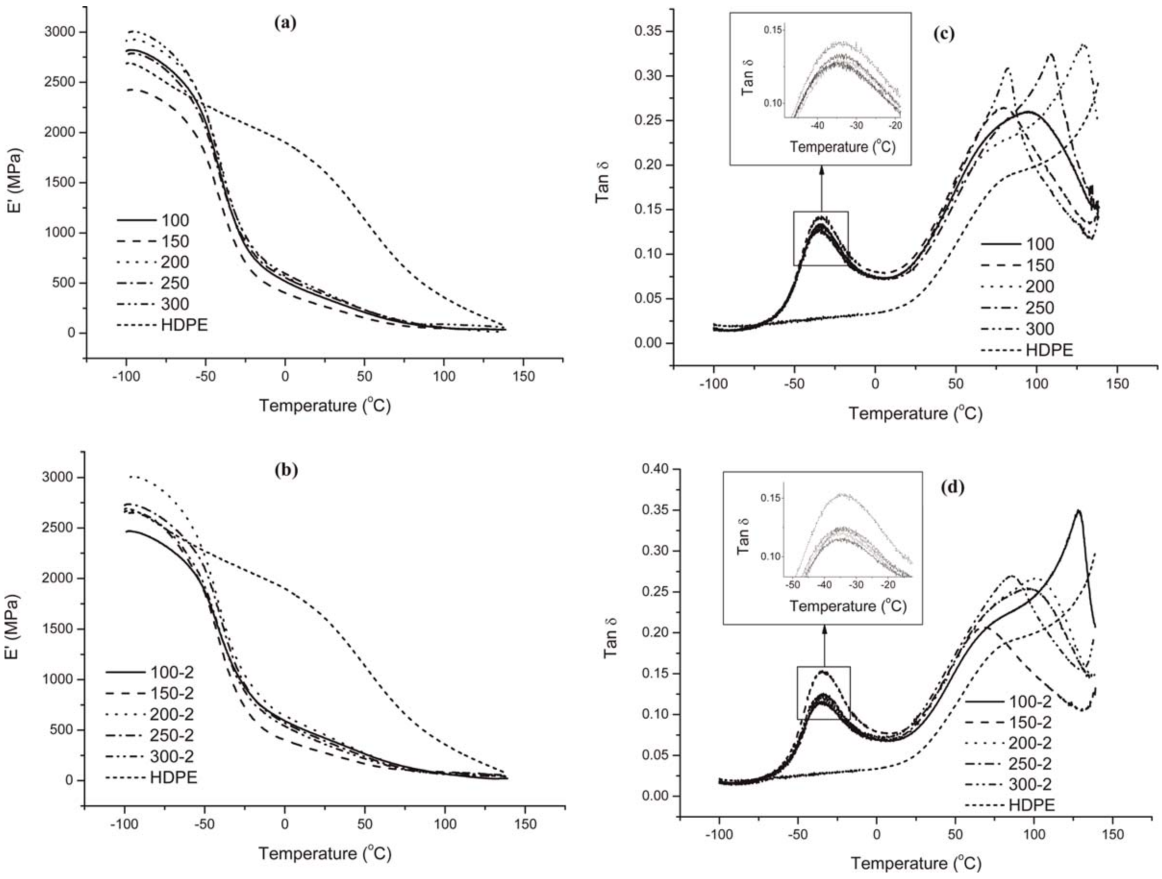

Figure 6. Dynamic mechanical properties of the blends produced through feeding modes 1 (a,c) and 2 (b,d): E' (a,b); and tan δ (c,d), where the inserts show an amplification of the T_g regions of the GTR.

elastomeric phase of the former to be more highly cross-linked. Those data validate the results obtained from the above dynamic mechanical analysis.

The storage modulus decreased as the size of rubber particles reduced, as confirmed by the SEM images. Since the morphology achieved through feeding mode 2 was finer, G' was expected to increase due to more efficient stress transfer between the phases. However, the results of elongation at break showed poorer adhesion between the phases of the blends, which probably caused a decrease in G'. The same behavior was previously observed,[5,50] and the authors correlated the decrease in G' with the deterioration of the mechanical properties of the blends of GTR devulcanized by microwaves and HDPE, due to particle detachment from the matrix when an external stress was applied.

In what follows, the effects of the processing parameters on the thermal properties of the HDPE phase are discussed.

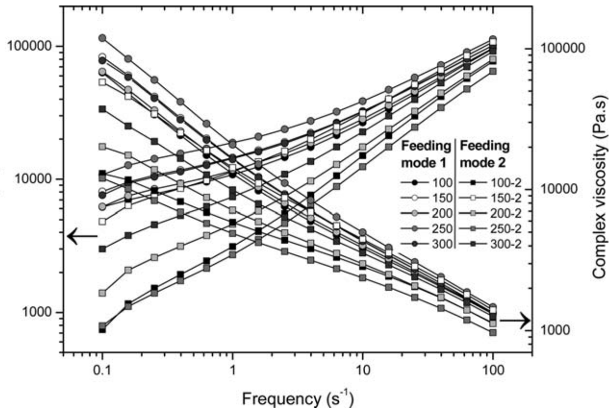

Figure 7. Evolution of G' and η^* of the blends produced through feeding modes 1 and 2.

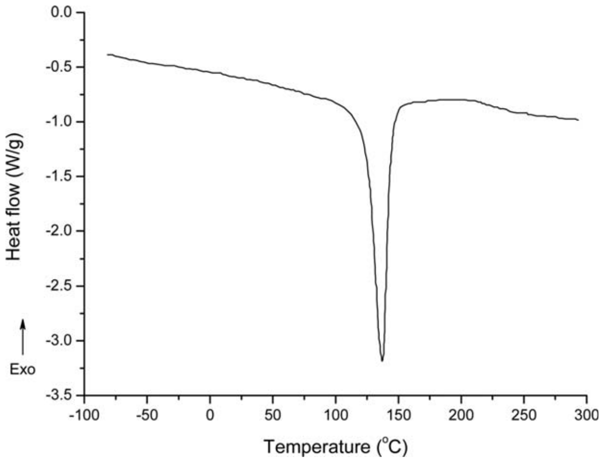

Figure 8. DSC scan (second heating cycle) of sample 100.

Table II. Values of Melting Temperature, Enthalpy of Melting (ΔH_m), and Crystallization Degree (X_c) of the HDPE Phase of the Blends

Feeding mode 1				Feeding mode 2			
Sample	T_m (°C)	ΔH_m (J/g)	X_C (%)	Sample	T_m (°C)	ΔH_m (J/g)	X_C (%)
100	137.4	101.6	86.7	100-2	131.5	89.7	76.6
150	136.2	97.6	83.3	150-2	136.7	101.0	86.2
200	135.0	96.3	82.2	200-2	136.0	104.4	89.1
250	135.3	110.6	94.4	250-2	135.0	112.5	96.0
300	136.3	106.9	91.2	300-2	137.3	104.6	89.3

Thermal Properties

Figure 8 shows the DSC curve (second heating cycle) of the sample 100. All other samples followed the same behavior. Table II shows the parameters calculated from the DSC curves of the blends (from the second heating cycle). The crystallization degree was calculated according to eq. (2)[61]:

$$X_c = \left[\frac{\Delta H_m}{(\Delta H_{m100} \cdot W_{HDPE})}\right] \cdot 100 \qquad (2)$$

where X_c is the crystallinity, ΔH_m is the enthalpy of melting (J/g), is the enthalpy of melting of the HDPE 100% crystalline (293 J/g)[62] and W_{HDPE} is the mass fraction of HDPE in blend.

For all blends, the melting temperatures of the HDPE phase did not change greatly. Nevertheless, its crystallinity was affected by the presence of the elastomeric phase (Table II). According to Lima *et al.*,[63] rubber components usually affect the crystallization process, influencing the nucleation mechanism and, thereby, the nucleation density and growth of spherulites. The rubber content, its molecular weight, and melt flow rate are some of the parameters that may hinder or induce the nucleation process.

In general, there was a tendency of increasing the enthalpy of melting and crystallinity of the HDPE phase as the screw speed increased, except in the extreme values of the screw speed (Table II). As the SEM images showed, there was a decrease in the particles diameter as the screw speed increased, especially in the case of feeding mode 2. According to Moly *et al.*,[64] an increase in the enthalpy of melting of a blend is due to the fact that the dispersed phase acted as nucleating agents, resulting in an increase in crystallinity. The same phenomenon probably happened in the blends of this work. In fact, the blends which showed the highest values of enthalpy of melting and crystallinity were the ones with the smallest rubber domain size (produced through feeding mode 2).

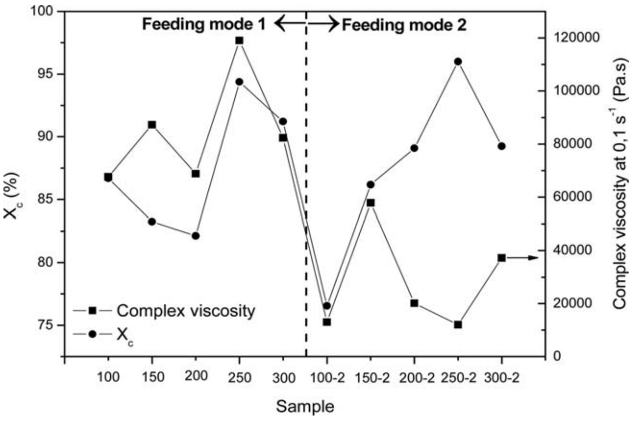

Figure 9. Crystallinity and complex viscosity values of the blends analyzed in this work.

Ponnamma *et al.*[65] investigated the crystallization behavior of HDPE in a NBR/HDPE blend, as well as the influences of the phase concentration, presence of compatibilizer and filler, and dynamic vulcanization. In the blends containing a small concentration of compatibilizer, the NBR domains were significantly reduced. Consequently, those small NBR particles acted as heterogeneous nuclei for crystallization, thereby causing an increase in crystallinity. Likewise, dynamic vulcanization resulted in the generation of a large number of small cross-linked rubber particles, which hindered the growth process of spherulites (their growth stopped when they touched a rubber particle). According to the authors, dynamic vulcanization decreased the crystallinity of the blends due to the co-cross-linking between the phases, which interfered in the orderly arrangement of the HDPE chains. They hypothesized that the co-cross-linking probably influenced the mechanical properties of the blends and decreased the crystallinity. Lima *et al.*[63] reported an increase in the crystallinity of polypropylene phase as a result of GTR addition. According to them, GTR had a strong nucleating effect.

It is more difficult for polymers with high viscosity to crystallize because of low molecular mobility.[66] Such a behavior was observed in the blends produced by feeding mode 2 (Figure 9). A decrease in complex viscosity resulted in an increase in crystallinity. As a conclusion, the blends with the highest crystallinities are those with the lowest complex viscosities, and smallest spherulites (their growth was hindered by the cross-linked GTR particles finely dispersed in the HDPE matrix). Cross-linked GTR particles also lead to more effective heterogeneous nucleation in the HDPE phase.

As discussed earlier, the nucleating effects are the probable causes of differences in the dynamic mechanical properties.

CONCLUSIONS

The results found in this work clearly show the importance of the processing parameters (feeding mode and screw speed) involved in the production of blends of dynamically revulcanized rubber phase in a twin screw extruder, as well as the necessity of good match between the residence time of the rubber during processing and its revulcanization kinetics. Optimum processing conditions are responsible for fine morphology and good mechanical properties of the blend. For a highly cross-linked rubber, its residence time in the screw extruder is the most important factor.

The finest morphology and consequently the best mechanical properties were obtained when feeding mode 2 was used and the screw speed was high. Those processing conditions allowed matching the residence time with the revulcanization kinetics in such a way that the revulcanization of the rubber could happen at the same time as the high stress and strain rates were applied to the blend. Therefore, coalescence was avoided and the break-up of the particles was promoted. However, mechanical properties were still poor due to the insufficient compatibility and low adhesion between the phases.

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